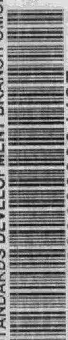


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SCIENTIFIC CRITERIA DOCUMENT FOR STANDARD DEVELOPMENT No. 2-84

CHLORINATED PHENOLS IN THE AQUATIC ENVIRONMENT

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**Ministry
of the
Environment**

The Honourable
Jim Bradley
Minister

Rod McLeod, Q.C.
Deputy Minister

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SCIENTIFIC CRITERIA
DOCUMENT FOR STANDARD
DEVELOPMENT No. 2-84

CHLORINATED PHENOLS
IN THE AQUATIC ENVIRONMENT

Prepared for

WATER RESOURCES BRANCH

Ontario Ministry of the Environment

by

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March 1984

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SUMMARY

Background

In this report, the chlorophenols (CP's) are divided into five major groups of isomers - monochlorophenols (MCP's), dichlorophenols (DCP's), trichlorophenols (TCP's), tetrachlorophenols (TTCP's) and pentachlorophenol (PCP). CP's are commercially used as biocides or as intermediates in biocide production. These compounds are introduced to surface water environments primarily in discharges from forest products industries, sewage treatment plants and agricultural systems.

Because of their toxic properties and potentially widespread occurrence in the environment, the need to establish criteria for the protection of aquatic ecosystems was recognized. This report reviews the behaviour and toxicity of CP's in freshwater environments, and recommends criteria for the protection of aquatic life in freshwater ecosystems from CP contamination.

Environmental Fate

Table 1 provides an overview of the relative importance of various environmental processes affecting the removal and breakdown of CP's in surface waters. These processes may be divided into two groups - degradation processes that alter the chemical structure of CP's and transport processes that remove CP's from the water column.

Among degradation processes, biodegradation by microorganisms appears to be the most important breakdown process for all CP's. Rates of biodegradation depend on water quality conditions (temperature, flow, dissolved oxygen level) and generally increase with increasing chlorination of the phenol ring (Alexander and Aleem 1961). Photolysis may be a significant degradation process for PCP in shallow, neutral to alkaline waters. Photolysis of other CP isomers has been reported, but its importance under environmental conditions is unknown. Chemical degradation without microbial or photolytic processes is thought to be insignificant in the environment.

The two abiotic transport processes considered are sorption and volatilization. All CP's tend to adsorb onto particulates in the water column, especially where the particulate organic level is high. Enrichment of nearly all isomers in sediments has been observed in

TABLE 1: SUMMARY OF AQUATIC FATE OF CHLOROPHENOLS

	<u>Monochlorophenols</u>	<u>Dichlorophenols</u>	<u>Trichlorophenols</u>	<u>Tetrachlorophenols</u>	<u>Pentachlorophenol</u>
<u>Degradation Processes</u>					
Photolysis	demonstrated in laboratory; environmental significance unknown.	probably insignificant in natural waters	process has been reported; environmental relevance unknown.	process apparently unreported for TTCP probably occurs to some extent; environmental relevance unknown.	of some importance in neutral to alkaline conditions, particularly in shallow, clear waters.
Biodegradation	reported in laboratory for all isomers; rate in environment uncertain	a well-substantiated process; rate depends on water quality and adaptation of bacteria.	reported in water, soil and bacterial cultures; probably occurs more readily in stagnant waters than in dilute or flowing systems.	reported in soil and bacterial cultures; TTCP persisted in sediment and water of a contaminated Mississippi lake, suggesting slow biodegradation in aquatic systems.	reported in aquatic conditions and in bacterial cultures; favoured by high temperatures and aerobic conditions.
Chemical Degradation	hydrolysis and oxidation considered unimportant.	oxidation and hydrolysis reactions are probably insignificant.	oxidation and hydrolysis reactions are probably insignificant.	oxidation and hydrolysis reactions are probably insignificant.	oxidation and hydrolysis reactions are probably insignificant.
<u>Transport Processes</u>					
Sorption	show some tendency to associate with particulates, based on log P values (2.19 to 250) and on observed sediment contamination in the Rhine River.	may be of some importance in organic particulates based on a log P of 2.75-3.08; sediment accumulation of various DCP's observed in Rhine River sediments.	probably important based on log P of 3.72 for 2,4,5- and 3.38 for 2,4,6-TCP; sediment enrichment observed in Rhine River and Finnish lake sediments.	probably important based on log P of 4.10 for 2,3,4,6-TTCP; sediment enrichment reported in a Mississippi lake, the Rhine River and a Finnish lake.	important based on log P of 5.01 (undissociated PCP); sorption more favoured under acidic conditions; sediment enrichment observed in contaminated environments.
Volatilization	probably of low environmental significance.	not considered important in natural surface waters.	not considered important in natural surface waters.	not considered important in natural surface waters.	probably of minor importance in shallow waters at pH 5; of negligible importance under neutral or alkaline conditions.
Bioaccumulation	theoretical BCF 7 to 70X based on log P, measured BCF in bluegill, 214 times.	reported in marine biota and crop plants; calculated BCF = 39 to 67 based on log P of 2.92	2,4,5-TCP: BCF = 170-1,900 (fish); 2,4,6-TCP: BCF = 51-4420 (plants), 115-12,180(fish), 3,000 (invertebrates).	BCF calculated from log P = 330-609 (fish); measured BCF, sunfish, bass, catfish - 20-221 (muscle), 40-8,590(liver), leeches - 10,000, <u>Cladophora</u> - 1,250.	measured BCF's range from 10 to 15,000 in fish, highest values in liver; whole body and muscle BCF $\leq$ 1,000 in most fish; up to 15,000 in Bay of Quinte fish, lower in algae and invertebrates; usually $\leq$ 500 for fish muscle; calculated BCF's based on log P of 5.01 are higher than measured values; BCF in algae = 1,250.
Probable Environmental Half-life	<1 - 26 days	$\geq$ 6 days	> 9 to $\geq$ 35 days	> 3.5 months, possibly years in organic-rich sediments	< 3.5 months (aerobic conditions) to years in organic-rich sediments.

the environment (e.g., Wegman and Broek 1983). The affinity of CP's for particulates increases somewhat with increasing chlorination. However, increasing pKa values with increasing chlorination indicate that the higher chlorinated compounds tend to be ionized at neutral pH, thereby reducing their octanol solubility (Hansch and Leo 1979). Consequently, their affinity for organic matter in sedimentary materials is also reduced. Volatilization of all CP's from the water column is probably of low importance for removal from the water column.

All CP's bioconcentrate in aquatic biota. Bioconcentration factors (BCF's) are highly variable, depending on the species studied and on experimental procedure. Calculated BCF values based on octanol-water partition coefficients suggest increasing BCF's with increasing phenol chlorination. BCF values are generally lower in MCP's and DCP's (up to about 200 X) than in the higher CP's, with the highest observed values exceeding 10,000 X (2,4,6-TCP). Observed BCF's usually do not exceed 1000 X for all CP's. Liver tissue is usually characterized by a higher BCF than those for muscle or whole fish. Rates of CP uptake from water are relatively rapid in fish. When returned to clean water, the depuration of CP's by fish is relatively rapid for MCP and DCP ($T_{1/2} < 2$ days), but may be slower for TCP, TTCP and PCP ($T_{1/2} < 10$ days).

Overall half-lives for CP's in aquatic environments, based primarily on biodegradation, are relatively short. Half-lives appear to range from days for MCP and DCP to weeks for TCP and months for TTCP and PCP (Table I).

Effects on Aquatic Organisms

Table 2 summarizes the lowest criteria reported for acute and chronic toxicity in aquatic animals, toxicity to plants and flesh-tainting thresholds for the five CP isomer groups. The most obvious trend illustrated in this table is the increasing acute toxicity with increasing chlorination. Thus, the lowest LC₅₀ values for MCP's are 2100-3830 ug/L, and the lowest value for PCP is 55 ug/L. Fish flesh tainting thresholds also tend to decrease with increasing chlorination. Tainting thresholds for MCP and DCP are much lower than levels causing acute and chronic effects. Shumway and Palensky (1973) could not reach a tainting threshold for PCP in test fish without causing acute lethality.

Another important trend noted in specific studies, but not apparent in Table 2, is a decrease in CP toxicity with increasing pH (e.g., Holcombe et al. 1980). CP's tend to

TABLE 2: SUMMARY OF LOWEST TOXICITY VALUES¹ (ACUTE, CHRONIC AND PLANT TOXICITY)
AND FLAVOUR IMPAIRMENT THRESHOLDS FOR CHLOROPHENOLS

Chlorophenol	Acute		Chronic		Plant		Tainting Threshold
	Value	Species	Value	Species	Value	Species	
Monochlorophenols							
2-CP	2100	rainbow trout	3900	fathead minnow	500 mg/L	green alga	15
3-CP	2900	rainbow trout	-	-	-	-	15
4-CP	3830	bluegill	-	-	4790	duckweed	15
Dichlorophenols							
2,4-DCP	1480	goldfish	70	rainbow trout	50 mg/L	green alga	0.4
Trichlorophenols							
2,3,5-TCP	450	bluegill	-	-	10 mg/L	green alga	-
2,3,6-TCP	320	bluegill	720	fathead minnow	5920	duckweed	52
Tetrachlorophenols							
2,3,4,6-TTCP	140	bluegill	-	-	603	duckweed	-
2,3,5,6-TTCP	170	bluegill	-	-	2660	green alga	-
Pentachlorophenol	55	coho salmon	1.61	sockeye salmon	7.5	green alga	-

¹All values expressed in ug/L unless otherwise indicated.

dissociate to chlorophenate ions in water and the degree of dissociation depends on both the pH of the water and on the dissociation constant of the specific CP isomer. The degree of dissociation increases with pH. The lower CP's do not dissociate as readily as the higher CP's at normal environmental pH. Because the dissociated forms of CP's are considerably less toxic than the undissociated forms, increasing pH tends to decrease CP toxicity.

Although few studies have examined the effect of water hardness on CP toxicity, the available data indicate that toxicity is not appreciably diminished by increasing hardness (e.g., Birge *et al.* 1979).

Recommended Criteria

The surface water quality criteria recommended for the protection of aquatic biota are summarized in Table 3. These values are based on acute and chronic toxicity data and on threshold concentrations for the tainting of fish flesh. All values are derived to protect the most sensitive Ontario species from both toxicity (acute and chronic) and flavour impairment.

The most sensitive response of aquatic biota to MCP and DCP is flavour impairment. Recommended criteria are, therefore, less than the lowest tainting thresholds for these lower CP's. The conventional approach of using acute toxicity data and standard application factors to derive criteria would not protect aquatic biota from flavour impairment.

The recommended criterion for TCP is based on the lowest acute LC₅₀ value multiplied by an application factor of 0.05 for non-persistent contaminants. Non-persistent toxic contaminants are those having half-lives in surface water environments of less than eight weeks, as stipulated by the International Joint Commission in the Great Lakes Water Quality Agreement of 1978.

Recommended criteria for TTCP and PCP are based on the lowest acute LC₅₀ values multiplied by an application factor of 0.01 for persistent contaminants. Persistent toxic contaminants, as defined by the International Joint Commission, have half-lives of greater than eight weeks in surface water environments.

TABLE 3: RECOMMENDED SURFACE WATER CRITERIA FOR CHLOROPHENOLS

Chlorophenol	Recommended Criterion ¹ (ug/L)	Basis
Monochlorophenols	7	flavour impairment
Dichlorophenols	0.2	flavour impairment
Trichlorophenols	18	acute toxicity, non-persistent
Tetrachlorophenols	1	acute toxicity, persistent
Pentachlorophenol	0.5	acute toxicity, persistent

¹Criteria are applicable to all isomers within each chlorinated class.

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Appendix I: Guidelines for Toxicity Data Used
in Criteria Development

Appendix II: Taste and Odour Impairment by Chlorophenols
in Drinking Water

1.0 INTRODUCTION

1.1 Background

The chlorophenols (CP's) considered in this report include five major groups of isomers - mono-, di-, tri-, tetra-, and pentachlorophenol. Members of each group have commercial utility. CP's are used commercially as biocides or as intermediates in the production of biocides, including bactericides, antiseptics, disinfectants, slimicides, fungicides, herbicides, insecticides, and wood and glue preservatives.

CP's are introduced to freshwater systems discharges from wood preserving industries, pulp and paper operations, sewage treatment plants and agricultural systems. They may also be formed during the chlorination of water or wastewater containing phenol. Also, CP's may form from the decomposition of chemically-related substances such as CP's and biocides manufactured from CP's.

Because of the inherent toxic properties and potentially widespread occurrence of CP's in the environment, the need to establish criteria for the protection of provincial surface waters from CP contamination was recognized by the Ontario Ministry of the Environment. The objectives of this report are to review the behaviour and toxicity of CP's in freshwater environments and, subsequently, to develop criteria for the protection of aquatic life in freshwater ecosystems from deleterious effects due to CP contamination.

These criteria are intended to provide the scientific rationale for the development of the Ministry's Provincial Water Quality Objectives for CP's. Objectives are defined as "a set of narrative and numerical criteria designed for the protection of aquatic life and recreation in and on the water. They represent a desirable level of water quality that the Ministry strives to maintain in surface waters of the Province" (Ontario Ministry of the Environment 1978).

1.2 Environmental Fate

Once released to surface waters, the fate of CP's in the environment is controlled by several degradation and transport processes. Degradation processes include photolysis,

biodegradation and chemical degradation. Aquatic transport processes considered here are grouped into volatilization, sorption and bioaccumulation. This report reviews the behaviour of CP's in surface water systems by major isomer groups. An effort is made to quantify environmental persistence and bioaccumulation in aquatic biota, and to describe the importance of environmental sinks for CP's. Persistence in the environment and in biota influences the degree of hazard presented by CP contamination and, consequently, affects the approach followed in the formulation of criteria.

To standardize the comparability among isomers with respect to persistence of accumulated contaminants in aquatic organisms, a theoretical approach developed by Neely (1979) was used to estimate the rate of clearance (depuration) of each CP group by a "standard" 500 g rainbow trout at 15°C in oxygen-saturated water. This approach is based on published species-specific metabolic rates, body weight, dissolved oxygen content of the water, and on the lipophobicity and bioconcentration factor of the CP, as estimated by octanol-water partition coefficients. Uptake rate constants, k_1 , in units of mL of water per gram of fish per hour, are also estimated. These values may be multiplied by a concentration of contaminant in water to derive an uptake rate in units of mass of contaminant per gram of fish per hour.

1.3 Effects on Aquatic Organisms

The toxic effects of CP's on aquatic biota are variable, and depend on the specific CP isomer as well as on the species tested. Other water quality parameters, particularly pH, may influence the toxicity of CP's to aquatic organisms (e.g. Saarikoski and Viluksela 1981). In general, toxicity tends to increase with the degree of chlorination, as shown in data compiled by the U.S. Environmental Protection Agency (U.S. EPA 1980a). Acute lethality is of environmental relevance, as "fish kills" have been attributed to PCP and TTCP contamination in freshwater environments (e.g. Mackenzie et al. 1975). Acute lethality from CP contamination in Ontario is apparently unreported.

Flavour impairment of fish flesh by CP contamination is well documented (Shumway and Palensky 1973). Because fish tainting impairs the use of aquatic resources, tainting thresholds are considered in the formulation of water quality criteria for CP's.

A primary objective of this study was to compile an extensive data base on the effects of CP's on aquatic biota for the subsequent derivation of water quality criteria. This was accomplished by undertaking a thorough review of the scientific literature on CP toxicology.

In this report, aquatic effects are divided into acute and chronic toxicity to fish and invertebrates, toxicity to aquatic plants (including both algae and macrophytes) and flavour impairment in fish. Criteria are derived to protect the most sensitive aquatic biota from acute or chronic responses or flavour impairment due to CP contamination.

The data base on the acute and chronic toxicity is large, and encompasses a diversity of study designs and test species. To permit a comparative evaluation among tests and species most applicable to the Ontario environment, toxicity data were selected for further consideration on the basis of the general guidelines outlined in Appendix I. These guidelines are similar to those used by the U.S. EPA for water quality criteria formulation (Federal Register 1980). Acute and chronic data were subdivided into primary and secondary data on this basis.

1.4 Criteria Development

A standard approach was adopted for the formulation of surface water criteria for CP's from the compiled data bases. The approach is designed to protect the most sensitive use of aquatic ecosystems against CP contamination. The recommended criteria represent maximum concentrations in surface waters that should not evoke any acute or chronic response in the most sensitive aquatic organisms, and should not cause any impairment of flavour in fish flesh. The following procedures were followed in the criteria development process:

1. The lowest species-specific geometric mean LC_{50} value for the most toxic CP isomer in each group (i.e., MCP's, DCP's, etc.) was selected from the acute toxicity data base.
2. The persistence of each CP group in the aquatic environment was identified on the basis of estimates of their half-lives in surface water ecosystems. Persistent compounds were defined as CP's having a half-life of greater

than eight weeks, based on the definition of persistence adopted by the International Joint Commission in the Great Lakes Water Quality Agreement of 1978.

3. The lowest species-specific geometric mean acute LC_{50} was multiplied by an application factor (AF) of 0.05 for non-persistent contaminants, or 0.01 for persistent contaminants to derive the product "C". This approach to the derivation of water quality criteria is consistent with the intent of the "Water Management Goals, Policies, Objectives and Implementation Procedures of the Ontario Ministry of the Environment (1978).
4. The lowest fish flesh tainting concentration, "T", was lowered by 50% (i.e., 0.5T) to provide protection against tainting. The reduction of T by 50% was arbitrarily selected to estimate a concentration that would not cause tainting.
5. Acute, chronic and tainting data for each isomer were plotted on semi-logarithmic graph paper. Following the procedures described above, values for C and 0.5T were calculated.
6. The lower of C and 0.5T was used for the final criterion selection and compared with chronic data to ensure adequate protection was afforded. Only in the case of PCP did chronic effect concentrations approach the tentatively selected criterion.

The toxicity of CP's to aquatic biota is dependent on pH (e.g. Saarikoski and Viluksela 1982). However, quantitative relationships between pH and toxicity applicable to a diversity of species found in Ontario are not available. Thus, pH-specific criteria, such as those adopted for ammonia (Ontario Ministry of the Environment 1979) are not derived for CP's.

The criteria developed in this report are for the protection of the aquatic ecosystem. However, taste and odour thresholds for CP's in drinking water are listed in Appendix II, and are plotted in Figures 2-1, 3-1, 4-1, 5-1 and 6-1 for ease of reference.

2.0 MONOCHLOROPHENOLS

Three isomers of monochlorophenol are found:

2-chlorophenol (2-CP)	Other names	<u>o</u> -chlorophenol
3-chlorophenol (3-CP)		<u>m</u> -chlorophenol
4-chlorophenol (4-CP)		<u>p</u> -chlorophenol

2.1 Occurrence

Only two of the three monochlorophenols (MCP's), 2-CP and 4-CP, are in general use by industry (Jones 1981). The third isomer - 3-CP - has limited commercial use. None of the three isomers are manufactured in Canada. Principal suppliers of MCP's to the Canadian market, according to data compiled by Jones (1981), are:

3-CP, 2-CP

Bayer (Canada) Ltd.
7600 Trans-Canada Highway
Pointe Claire, Quebec
H9R 1C8

4-CP

Bayer (Canada) Ltd.
through Japan Chemicals Ltd.
940 Alness St. Unit 10
Downsview, Ontario
M3J 2R9

MCP's have been used as antiseptics since 1893 (von Oettingen 1949). 2-CP and 4-CP are intermediate feedstocks in the manufacture of higher chlorophenols and chlorocresols for biocide production. 2-CP is also used to form intermediates in the production of phenolic resins and has been utilized in the extraction of sulphur and nitrogen compounds from coal (U.S. EPA 1980a).

MCP's may be formed inadvertently in the chlorination of effluent or drinking water containing phenol. The chlorination of phenol in dilute aqueous solutions and in sewage effluents has been demonstrated by Aly (1968), Barnhart and Campbell (1972), Jolley

(1973) and Jolley et al. (1975). Both 3-CP and 4-CP have been identified in chlorinated samples of primary and secondary sewage treatment plant effluents (U.S. EPA 1975). Jolley et al. 1975 measured levels in secondary sewage effluents of 1.7, 0.5 and 0.7 ug/L for 2-3- and 4-CP respectively. MCP's may also be present in pulp and paper effluents (Environment Canada 1979a) and in wastes from the wood preservation industry.

Various CP compounds and isomers are produced as intermediate metabolites in the microbial breakdown of the herbicides 2,4-D and 2,4,5-T and pesticides Silvex ^R, Ronnel ^R, lindane and benzene hexachloride (U.S. EPA 1980a). MCP's may be formed in the environment in this manner.

The range of use and production suggests that this group is introduced to the environment both from point sources (industrial and municipal effluents) and from non-point sources (e.g. breakdown and mobilization of pesticides). Thus the potential distribution of these compounds in Ontario waters is wide.

2.2 Environmental Fate

2.2.1 Physical and Chemical Properties

A summary of the physicochemical properties of MCP's is presented in Table 2-1. These properties govern the behaviour of these chemicals in surface water systems.

2.2.2 Photolysis

The photochemical behaviour of MCP's in dilute aqueous solutions was studied by Boule et al. (1982). Photodegradation depends on the position of chlorine on the benzene ring. In molecular form, 2-CP is converted to pyrocatechol, while in anionic form, it is reduced to a cyclopentadienic acid which dimerizes. Irradiation of 3-CP leads to resorcinol at any pH, while 4-CP is converted to hydroquinone in combination with poly-phenolic oligomers. Yasuhara et al. (1977) reported that 2- and 3-CP were subject to photodegradation in the presence of hydrogen peroxide, while 4-CP decomposed readily without the catalyst. However, the importance of photodegradation in natural waters where photosensitizers and inhibitors may be present is unknown. Crosby (1972a,b) reviewed the photo-oxidation of pesticides in the environment.

2.2.3 Microbial Degradation

Chlorophenols are generally more stable to biodegradation than phenol, and resistance to degradation is greatest among the more highly chlorinated phenols (Alexander and Aleem 1961). Ettinger and Ruchhoft (1950) reported incomplete removal of 1 mg/L, 2-CP and 4-CP in dilute sewage over 20 to 30 days at 20°C, but observed removal of similar amounts during the same period in polluted river water. They concluded that specialized microflora are required for biodegradation. Ingols *et al.* (1966) reported 100% degradation of the ring structure of 2-, 3- and 4-CP in two to three days by acclimated activated sludge at MCP levels of 100 mg/L. Walker (1973) reported metabolism of 2-, 3- and 4-CP by yeasts isolated from soil. Activated sludge bacteria removed 95.6% and 96% of 2-CP and 4-CP respectively, over 20 days when these compounds provided the only source of carbon (Pitter 1976). At concentrations of 1 to 10 mg/L in laboratory cultures, 2-CP is completely degraded by various bacteria in 3 to 6 hours (Loos *et al.* 1967; Baird *et al.* 1974), although at higher concentrations (100 mg/L), only 20% is degraded over this period (Baird *et al.* 1974). Kreuk and Hanstveit (1981) reported 70% degradation of 4-CP at initial levels of 1 mg/L over 3 to 45 days in seawater and over 9 to 26 days in a nutrient medium. In general, para-chlorophenols appear more liable to microbial degradation than ortho- and meta-substituted forms (Buikema *et al.* 1979).

The U.S. EPA (1979) stated that genetic induction levels for most degradative organisms may not be attained in receiving waters except near discharges. Thus, the degree of microbial degradation of MCP's in the natural environment will probably increase under stagnant or slow-flowing conditions and decrease under rapid dilution conditions. Based on laboratory studies reported in the literature, it seems reasonable to expect that the half-life of MCP's due to biodegradation in surface waters is within the range of 1 to 26 days.

2.2.4 Chemical Degradation

Information on the importance of chemical degradation of MCP's in natural waters is unavailable. Hydrolysis of these compounds is probably unimportant due to the high resistance of substituents attached to aromatic rings to hydrolysis (Morrison and Boyd

1973). Hydroxyl radicals may attack 2-CP at the C-2 and C-4 positions, but information on oxidation reaction rates in the environment is lacking. The National Research Council of Canada (NRCC 1982) suggested that oxidation of CP's requires further study.

2.2.5 Sorption Processes

Wegman and Broek (1983) reported MCP levels in sediment and water in the Rhine River mouth. Maximum observed concentrations were:

	<u>Sediment (ug/kg, dry weight)</u>	<u>Water (ug/L)</u>
2-CP	10	0.6
3-CP	43	3.4
4-CP	10	2.1

These data suggest some accumulation in sediment for 3-CP. However, low frequencies of occurrence of 3-CP in sediment (6% of samples) and the absence of detectible 2-CP and 4-CP may indicate removal from the water by other process (e.g. photolysis and biodegradation) before significant sediment accumulation occurs. The author's cautioned, however, that their detection limits for MCP's were relatively high.

Values for log octanol/water partition coefficients for 2-, 3- and 4-CP, calculated using additivity principles illustrated by Neely et al. (1974) for MCP's are 2.19, 2.50 and 2.44, respectively. These log P values indicate a slight tendency for MCP's to associate with organic materials in sediments and suspended particulates, based on relationships between octanol-water partitioning and organic carbon content of sediment (Karickhoff et al. 1979). The U.S. EPA (1979) concluded that sorption of MCP's to clays in surface waters will not be significant.

2.2.6 Volatilization

Specific data on volatilization of MCP's from water are apparently lacking. Vapour pressures of MCP's are moderate to low, and their water solubilities are high (Table 2-1), thus volatilization probably occurs only very slowly. Furthermore, these compounds are somewhat acidic and thus are probably highly solvated in water, further decreasing the tendency to volatilize. The U.S. EPA (1979) surmised that volatilization is probably not an important removal process for 2-CP in water. Because of the lower vapour pressures

of 3-CP and 4-CP, these compounds are also unlikely to volatilize significantly from surface waters.

2.2.7 Bioaccumulation

The U.S. EPA (1980b) cited a bioconcentration factor for 2-CP in bluegill of 214 relative to water concentration. This experiment was run over 28 days at an exposure level of 9.2 ug/L. The rate of depuration was fast, with a half-life in the body of less than one day. Information on bioaccumulation of other MCP's in aquatic biota is lacking. Based on log P values of 2.19 to 2.50 for the three isomers, and on various relationships between log P and bioconcentration factors (Neely *et al.* 1974; Veith *et al.* 1979; Mackay 1982), theoretical bioconcentration factors for MCP's are approximately 7 to 38 times the concentration in the dissolved phase (Table 2-2).

Assuming the mean calculated bioconcentration factors 16 for 2-CP, 27 for 3-CP and 24 for 4-CP (Table 2-2), the following uptake and clearance rate constants are calculated on the basis of Neely's (1979) model:

	<u>Uptake Rate (k_1)</u>	<u>Fractional Clearance Rate (h^{-1})</u>
2-CP	1.5	0.095
3-CP	1.8	0.065
4-CP	1.7	0.072

These estimated clearance rates represent predicted residence times in fish tissues of 11 to 15 hours. Although a constant depuration rate is calculated, clearance of MCP's from tissues may decrease in rate as tissue contaminant levels become low.

Table 2-2 summarizes information on biological uptake and clearance of MCP's.

Given the relatively low bioconcentration factors and high depuration rates described here, we conclude that MCP's have a relatively low potential for accumulation in biota.

2.2.8 Probable Fate

Definitive information on the fate of MCP's in the environment is unavailable. Microbial degradation and photolysis have been reported in laboratory studies, but their relative environmental importance has not been assessed. Either or both of these processes may be important in the elimination of MCP's from surface waters. Removal by deposition with sediments may also be of some importance, particularly in depositional environments such as river mouths where suspended sediment loads are high. Based on observed rates of microbial degradation under laboratory conditions, half-lives of MCP's in surface waters probably range from less than 1 to 26 days. Table 2-3 summarizes the aquatic fate of MCP's.

2.3 Distribution In Ontario

Information on environmental levels of MCP's in Ontario is apparently lacking. However, because these compounds are widely used or are formed during the chlorination of effluents, MCP's, especially 2-CP and 4-CP, may be common in Ontario surface waters.

2.4 Effects on Aquatic Organisms

The MCP's are the least toxic of the chlorinated phenolic isomer groups, reflecting a direct relationship between toxicity and the degree of chlorination. Most of the available toxicity data for MCP's have been acquired from laboratory bioassays conducted under static conditions. In the majority of these studies, contaminant values were calculated, rather than measured in the test vessels. In general, the MCP isomers are known to impair the flavour of fish at concentrations below toxicity levels (U.S. EPA 1980a).

Acute, chronic and other relevant toxicity data, considered in this review, are presented in Tables 2-4 to 2-9. A graphical summary is provided for convenient reference in Figure 2-1.

2.4.1 Acute Toxicity

There is a decided lack of good information on the 3- and 4-CP isomers. However, a

considerable number of acute bioassays have been conducted for 2-CP on fish and invertebrates (Tables 2-4 and 2-5). Only two of these were flow-through tests, with concentrations measured in the test vessels. Recorded 96-hour LC₅₀ values ranged from 2,100 ug/L for rainbow trout (PPRIC, 1979) to 20,170 ug/L for guppy (Pickering and Henderson, 1966). Geometric means of the toxicity values comprising these data are shown in Table 2-4, and the data is summarized relative to chronic effects and various regulatory standards in Figure 2-1. It is apparent that the less stringent bioassays (Table 2-5) were not as sensitive as the primary tests considered for this review of 2-CP. Limited toxicity information is available for 3-CP.

Environment Canada (1979a) experimenting on juvenile rainbow trout found a 96-hour LC₅₀ of 2,900 ug/L. Considerably more good data has been developed for 4-CP. Buccafusco et al. (1981) compared 2- and 4-CP toxicity to bluegill sunfish and found 4-CP to be more toxic, with an LC₅₀ value of 3,830 ug/L. Saarikoski and Viluksela (1981) investigated the effects of pH on the toxicity of 4-CP to guppies and showed that acute toxicity decreases with increasing pH. The geometric mean of LC₅₀ values in this study was 7,900 ug/L.

2.4.2 Chronic Toxicity

Chronic responses to MCP isomers have not been well investigated. The U.S. EPA (1978) reported on a study in which fathead minnows were exposed to various concentrations of 2-CP. No adverse effects to early life stages were observed at the highest concentration of 3,900 ug/L (Table 2-6). Phipps et al. (1981) conducted eight-day chronic survival studies on fathead minnows for 2-CP and found consistent LC₅₀ values of 6,340 ug/L (Table 2-7). These chronic values are high relative to the lowest LC₅₀ values reported for MCP's. However, the primary acute data show that fathead minnows are among the most resistant species (Table 2-4).

2.4.3 Plant Toxicity

The effects of MCP's on aquatic plants have been investigated to some extent. Huang and Gloyna (1968) studied the influence of 2-CP on chlorophyll reduction in Chlorella pyrenoidosa and a minimum effect level of 500 mg/L. The U.S. EPA (1978) reported a 96-hour bioassay using Selenastrum capricornutum in which 4,790 ug/L of 4-CP

interrupted all production. In addition, Blackwell et al. (1955) found that 283 mg/L of 4-CP caused chlorosis in duckweed (Lemna minor).

2.4.4 Flavour Impairment

All MCP isomers have been found to impair the flavour of fish. Concentrations causing tainting are generally two orders of magnitude below those levels which cause acutely toxic responses (Figure 2-1). Threshold concentrations recorded for rainbow trout and carp for all three isomers ranged between 15 and 60 ug/L. From the data provided in Table 2-9, it would appear that bluegills are less able to bioaccumulate 2-CP than rainbow trout or carp. These values suggest that tainting is the sensitive response affecting resource use.

2.4.5 Criteria Development

In 1980, the U.S. EPA derived criteria for the protection of aquatic life by means of two approaches. The first was a maximum 'not-to-exceed' level based on acute toxicity data, and the second was a 24-hour average level, based on chronic toxicity data. At the time of the EPA review, insufficient information was available for the development of criteria for all MCP isomers. Only an acute maximum criterion for 2-CP was established based on the response of Daphnia magna at 4,380 ug/L. More recent data for rainbow trout toxicity would suggest 2,900 ug/L as a more reasonable estimate of acute levels (PPRIC, 1979). Use of the standard application factor for non-persistent compounds times this lowest acute value would result in a criterion of about 100 ug/L. This criterion, however, would not protect against fish flavour impairment, the most sensitive response recorded to date. The lowest individual tainting threshold was 15 ug/L (Figure 2-1). It is recommended that in keeping with the approach outlined in Section 1.4, one-half of the lowest tainting threshold, rounded to 7 ug/L, be adopted as the criterion for MCP.

TABLE 2-1: PHYSICAL PROPERTIES OF SELECTED MONOCHLOROPHENOLS
(adapted from Jones 1981)

CAS No.	Compound	Commercial utility	Formula	Molecular Weight	Boiling point ^a (760 mm or as stated), °C	Melting point ^a (°C)	Dissociation constant ^b at 25°C, K _a
95578	2-CP	limited	C ₆ H ₅ ClO	128.56	174.9	9.0	3.2x10 ⁻⁹
108430	3-CP	limited	"	"	214	33	1.4x10 ⁻⁹
106489	4-CP	yes	"	"	219.75	43.2-43.7	6.6x10 ⁻¹⁰

Compound	pK ^{c,e}	pK ^d	Water Solubility, 20°C ^e	Density ^{f,g}	Vapour Pressure@°C	Log p ^h	Flash Pt. ^g °C	Appearance
2-CP	8.48	8.65	28.5 g/L	1.2634 ²⁰ / ₄	1 mm@12.1C	2.19	63.9	Light amber liquid
3-CP	9.08	9.12	2.6 g/L	1.268 ²⁵	1 mm@44.2C	2.50		crystals
4-CP	9.42	9.37	27.1 g/L	1.2651 ³⁰ / ₄	1 mm@49.8C	2.44	121.1	Needle-like, white to straw colored crystals

^a Weast (1974)

^b Doedens (1967)

^c Pearce and Simpkins (1968)

^d Farquharson et al (1958)

^e U.S. EPA (1980a,b)

^f Density is relative to water, the superscript indicates the temperature of the liquid and the subscript the temperature of the water to which the density is referred.

^g Sax (1975)

^h Neely et al. (1974)

TABLE 2-2: BIOCONCENTRATION FACTORS AND DEPURATION RATES FOR MONOCHLOROPHENOLS IN FRESHWATER BIOTA

	BCF	Depuration	Reference
<u>2-CP</u>			
Bluegill	214	$T_{1/2} < 24 \text{ h}$	1
Fish (calculated)	7		2
	15		3
	25	clearance rate = 0.095 h^{-1}	4,5
<u>3-CP</u>			
Fish (calculated)	15		2
	27		3
	38	clearance rate = 0.065 h^{-1}	4,5
<u>4-CP</u>			
Fish (calculated)	13		2
	24		3
	35	clearance rate = 0.072 h^{-1}	4,5

1 U.S. EPA (1980b)

2 Mackay (1982)

3 Veith et al. (1979)

4 Neely et al. (1974)

5 Neely (1979) (see text for assumptions)

TABLE 2-3: SUMMARY OF AQUATIC FATE OF MONOCHLOROPHENOLS
(adapted from U.S. EPA 1979)

Environmental Process	Summary Statement	Rate	Half Life	U.S. EPA's Confidence of Data
<u>Degradation Processes</u>				
Photolysis	- demonstrated in laboratory; environmental significance unknown.	-	-	low
*Biodegradation	- reported in laboratory for all isomers; rate in environment uncertain.	-	<1-26 days	low
Chemical Degradation	- hydrolysis and oxidation considered unimportant.	-	-	low
<u>Transport Processes</u>				
Volatilization	- probably of low environmental significance.	-	-	low
*Sorption	- show some tendency to associate with particulates, based on log P values (2.19 to 2.50) and on observed sediment contamination in the Rhine River.	-	-	low
Bioaccumulation	- theoretical BCF 7 to 70X based on log P, measured BCF in bluegill, 214 times.	-	<1 day for depuration	medium
Probable overall environmental half-life			<1-26 days	
*Probable dominant processes in degradation and removal.				

TABLE 2-4: PRIMARY ACUTE TOXICITY DATA FOR THE MONOCHLOROPHENOLS

Isomer Evaluated	Species	Method ¹	Individual Results (ug/L)	Test Laboratory Water Quality				Laboratory	Reference
				Geometric Mean (ug/L)	Mean pH	Mean Temp. (°C)	Hardness (as CaCO ₃ mg/L)		
2-CP	<u>Cladoceran Daphnia magna</u>	48hr-LC ₅₀ , S,U	7,430		-	-	-	-	Kopperman et al 1974
		48hr-LC ₅₀ , S,U	2,600	4,380	8.0	22	173	E.G&G Bionomics Mass.	LeBlanc 1980
	<u>Fathead Minnow Pimephales promelas</u>	96hr-TLm, S,U	11,630		7.5	25	20	R.A. Taft Sanitary Engg. Centre	Pickering & Henderson 1966 ³
		96hr-TLm, S,U	14,480		8.2	25	360		
		96hr-LC ₅₀ , FT, M	11,000		7.5	23	451	US EPA Env. Research Laboratory Duluth, Minn.	Phipps et al. 1981 ³
			13,000	12,460	7.5	23	45		
	<u>Bluegill Lepomis macrochirus</u>	96hr-TLm, S,U	10,000		7.5	25	20	R.A. Taft Sanitary Engg. Centre	Pickering & Henderson 1960 ³
		96hr-LC ₅₀ , S,U	8,400		-	25	-	-	Henderson et al. 1960
			6,590	8,210	7.2	22	40	E,G&G Bionomics, Mass.	Buccafusco et al. 1981 ^{2,3}
	<u>Rainbow Trout Salmo gairdneri</u>	96hr-LC ₅₀ , S,U	2,100	2,100	7.7	12	280	Pulp & Paper Research Inst. Pt. Claire, Que.	PPRIC 1979

TABLE 2-4: PRIMARY ACUTE TOXICITY DATA FOR THE MONOCHLOROPHENOLS (Cont'd)

Isomer Evaluated	Species	Method ¹	Individual Results (ug/L)	Geometric Mean (ug/L)	Test Laboratory Water Quality			Laboratory	Reference
					Mean pH	Mean Temp. (°C)	Hardness (as CaCO ₃ mg/L) ³		
2-CP	Goldfish <u>Carassius auratus</u>	96hr-TLm, S,U	12,370	12,370	7.5	25	20	R.A. Taft Sanitary Eng. Center	Pickering & Henderson 1966
	Guppy <u>Poecilia reticulata</u>	96hr-TLm, S,U	20,170	20,170	7.5	25	20	R.A. Taft Sanitary Eng.	Pickering & Henderson 1966 ³
3-CP	Rainbow Trout <u>Salmo gairdneri</u>	96hr-LC ₅₀ , S,U	2,900	2,900	7.7	12	280	Pulp & Paper Res. Inst. Pt. Claire, Que.	PPRIC 1979
4-CP	Cladoceran <u>Daphnia magna</u>	48hr-LC ₅₀ , S,U	4,060		-	-	-	E,G&G Bionomics, Mass.	LeBlanc 1980
		48 hr-LC ₅₀ ,S,U	4,820	4,420	-	-	-	-	Kopperman et al. 1974
	Bluegill <u>Lepomis macrochirus</u>	96hr-LC ₅₀ , S,U	3,830	3,830	7.2	22	40	E,G&G Bionomics, Mass.	Buccafusco et al 1981 ^{2,3}
	Guppy <u>Poecilia reticulata</u>	96hr-LC ₅₀ , Semi S,M	6,300 7,840 8,490 9,000	7,900	5.0 6.0 7.0 8.0	26 26 26 26	90 90 90 90	Dept. of Zool. Univ. of Helsinki Finland	Saarikoski and Viluksela 1981 ⁴
								"	"

¹Terms: FT = flow-through bioassay, Semi S.= Static bioassay with solution replacement, S = static bioassay, U = test tank concentrations unmeasured, M = test tank concentrations measured, SW = water of low hardness
MW = water of medium hardness, HW = water of high hardness

²Conductivity reported

³Alkalinity reported

⁴Major ions reported

TABLE 2-5: SECONDARY ACUTE TOXICITY DATA FOR THE MONOCHLOROPHENOLS

Isomer Evaluated	Species	Method ¹	Results (ug/L)	Test Laboratory Water Quality			Laboratory	Reference
				Mean pH	Mean Temp. (°C)	Mean Hardness (as CaCO ₃ mg/L)		
2-CP	<u>Goldfish</u> <u>Carassius auratus</u>	8hr-LC ₄₂ , S,U	31,000	-	-	-	-	Gersdorff & Smith 1940
		8hr-LC ₆₂ , S,U	20,600	-	-	27	-	
		24hr-LC ₅₀ , S,U	16,000	-	-	-	-	Kobayashi <u>et al.</u> 1979
	<u>Bluegill</u> <u>Lepomis macrochirus</u>	48hr-LC ₅₀ , S,U	8,100	-	-	20	Dept. of Biol. Science, Purdue Univ., Indiana	Lammering & Burbank 1961
		24hr-LC ₅₀ , S,U	8,200	20	-	-		
3-CP	<u>Rainbow Trout</u> <u>Salmo gairdneri</u>	48hr-LC ₅₀ , FT,U	10,000	7.5	15	SW	Oak Creek Fish. Lab., Oregon State Univ. Corvallis	Shumway & Palensky 1973
	<u>Goldfish</u> <u>Carassius auratus</u>	8hr-LC ₆₂ , S,U	20,600	-	-	27	-	Gersdorff & Smith 1940
4-CP	<u>Goldfish</u> <u>Carassius auratus</u>	8hr-LC ₅₄ , S,U	6,300	-	-	-	-	"
		24-hr-LC ₅₀ , S,U	9,000	-	-	-	-	Kobayashi <u>etal.</u> 1979

¹Terms: FT = flow-through bioassay, Semi S.= Static bioassay with solution replacement, S= static bioassay, U = test tank concentrations unmeasured, M = test tank concentrations measured, SW = water of low hardness, MW = water of medium hardness, HW = water of high hardness

TABLE 2-6: PRIMARY CHRONIC TOXICITY DATA FOR THE MONOCHLOROPHENOLS

Isomer Evaluated	Species	Method ¹	<u>Test Laboratory Water Quality</u>					Laboratory	Reference
			Test Conc. Ranges (ug/L)	Conc. of Lowest Chronic Effect (ug/L)	Mean pH	Mean Temp. (°C)	Hardness (as CaCO ₃ mg/L)		
2-CP	Fathead Minnow <u>Pimephales promelas</u>	Early Life Stage	-	>3,900	-	-	-	-	U.S. EPA 1978

¹Terms: FT = flow-through bioassay, Semi S.= Static bioassay with solution replacement, S = static bioassay, U = test tank concentrations unmeasured, M = test tank concentrations measured, SW = water of low hardness MW = water of medium hardness, HW = water of high hardness

TABLE 2-7: SECONDARY CHRONIC TOXICITY DATA FOR THE MONOCHLOROPHENOLS

Isomer Evaluated	Species	Method ¹	Results (ug/L)	Test Laboratory Water Quality			Laboratory	Reference
				Mean pH	Mean Temp. (°C)	Hardness (as CaCO ₃ mg/L)		
2-CP	Fathead Minnow <u>Pimephales</u> <u>promelas</u>	8 day LC ₅₀ , FT, M	6,340	7.5	23	45	U.S. EPA Env. Res. Lab. Duluth, Minn.	Phipps <u>et al.</u> ³ 1981
			6,340	7.5	23	45		

¹Terms: FT = flow-through bioassay, Semi S.= Static bioassay with solution replacement, S = static bioassay,
U = test tank concentrations unmeasured, M = test tank concentrations measured, SW = water of low hardness
MW = water of medium hardness, HW = water of high hardness

²Conductivity reported

³Alkalinity reported

TABLE 2-8: PLANT VALUES FOR MONOCHLOROPHENOLS

Isomer Evaluated	Species	Method	Results (ug/L)	Test Laboratory Water Quality			Laboratory	Reference
				Mean pH	Mean Temp. (°C)	Mean Hardness (as CaCO ₃ mg/L)		
2-CP	Alga <u>Chlorella pyrenoidosa</u>	Chlorophyll reduction within 72 hours	500,000	7.3	25	-	Civil Engineer. Dept., Univ. of Texas	Huang & Gloyna 1967
4-CP	Alga <u>Selenastrum capricornutum</u>	96 hr-EC ₅₀ cell production	4,790	-	-	-	-	U.S. EPA 1978
	Duckweed <u>Lemna minor</u>	Chlorois 72 hr-LC ₅₀	282,830	5.1	25	-	Dept. of Agric., Oxford Univ., England	Blackman <u>et al.</u> 1955

TABLE 2-9: FISH TAINING VALUES FOR THE MONOCHLOROPHENOLS

Isomer Evaluated	Species	Method ¹	Test Laboratory Water Quality				Laboratory	Reference
			Est. Flavour Impairment Threshold (ug/L)	Mean pH	Mean Temp. (°C)	Mean Hardness (as CaCO ₃ mg/L)		
2-CP	Rainbow Trout <u>Salmo gairdneri</u>	ETC,FT,U	60	7.5	15	SW	Oak Cr. Fisher. Lab., Oregon St. Univ., Corvallis	Shumway & Palensky, 1973 ^{2,4}
	Bluegill <u>Lepomis macrochirus</u>	7 day exposure	2,000	-	-	-	-	Henderson <u>et al.</u> 1961
	Carp <u>Cyprinus carpio</u>	flesh tainting	15	-	-	-	-	EIFAC, 1973 (Schulze, 1961)
3-CP	Carp <u>Cyprinus carpio</u>	flesh tainting	60	-	-	-	-	EIFAC, 1973 (Schulze, 1961)
	Rainbow Trout <u>Salmo gairdneri</u>	ETC,FT,U	45	7.5	15	SW	Oak Cr. Fisher. Lab., Oregon St. Univ., Corvallis	Shumway & Palensky, 1973 ^{2,4}
4-CP	Carp <u>Cyprinus carpio</u>	flesh tainting	60	-	-	-	-	EIFAC, 1973 (Schulze, 1961)

¹ Terms: ETC = estimated threshold concentrations, SW = low water hardness, FT = flow-through bioassay, U = test tank concentrations measured

² Conductivity reported

³ Alkalinity reported

⁴ Major ions reported

3.0 DICHLOROPHENOLS

Ten isomers of dichlorophenol (DCP) may occur:

2,4-dichlorophenol (2,4-DCP)	3,5-dichlorophenol (3,5-DCP)
2,3-dichlorophenol (2,3-DCP)	3,6-dichlorophenol (3,6-DCP)
2,5-dichlorophenol (2,5-DCP)	4,5-dichlorophenol (4,5-DCP)
2,6-dichlorophenol (2,6-DCP)	4,6-dichlorophenol (4,6-DCP)
3,4-dichlorophenol (3,4-DCP)	5,6-dichlorophenol (5,6-DCP)

3.1 Occurrence

Of the ten isomers of dichlorophenol, only 2,4-DCP is in use as a primary chemical (U.S. EPA 1980c). 2,4-DCP is distributed in Canada by:

Bayer (Canada) Ltd.
through Dow Chemical of Canada Ltd.
P.O. Box 1012, Highway No. 40,
Sarnia, Ontario
N7T 7K1

and was manufactured (until July 1983) by:

Uniroyal Limited
Clover Bar, Alberta

All of the 2,4-DCP produced in Canada is used as an intermediate in the manufacturing of 2,4-D phenoxy herbicides (Jones 1981). Elsewhere, this compound is also used as a chemical intermediate in the production of germicides, temporary soil sterilants, plant growth regulators, moth-proofing agents, seed disinfectants, miticides and wood preservatives (U.S. EPA 1980c).

The formation of 2,4-DCP as a breakdown product of the herbicides 2,4-dichlorophenoxyacetic acid (2,4-D) and 2,4-dichlorophenyl p-nitrophenyl ether (Nitrofen) by photolysis and by microbial breakdown is well documented (eg. Nakagawa and Crosby 1974a,b; Zepp

et al. 1975; Alexander and Aleem 1961; Loos et al. 1967; Sharpee 1973; U.S. EPA 1980c). Several intermediates including 2,4-DCP are formed in the microbial metabolism of 2,4-D (see U.S. EPA 1980c). Kearney and Kaufman (1972) have shown that 2,4-DCP is an intermediate metabolite in the eventual degradation of 2,4-D to catechol intermediates and finally to succinic acid. Thus, herbicides may provide a diffuse source of 2,4-DCP to aquatic environments through runoff and erosion.

Other DCP's are also formed during the breakdown of pesticides. Crosby and Wong (1973) observed the formation of 2,5-DCP as a photolytic product of 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) in aerated water. In soil, 3,4- and 3,5-DCP have been found formed as breakdown products of pentachlorophenol (Ahlborg and Thunberg 1980). Similar processes may occur in aquatic systems, although the importance of these processes as sources of DCP contamination in surface waters is unknown.

CP's are widely used as anti-microbial or preserving agents in the wood processing industry. Jones (1981) provides a description of specific CP sources in wood preserving facilities. Unfortunately, effluents from Canadian wood preserving plants have not been characterized with respect to levels of specific CP isomers (Jones 1981) and thus, the degree of pollution by DCP's in process effluents is unknown.

DCP's may be formed in effluents from the bleaching of wood pulp by the pulp and paper industry. In a survey of the formation of chlorinated organics in pulp chlorination, Environment Canada (1979a) reported 2,4-DCP in laboratory-prepared effluents obtained from the bleaching of softwood and hardwood pulps. Bacon (1978) identified 2,4-DCP in effluent from a St. John, New Brunswick kraft mill. Robinson and Smillie (1977) reported 4 ug/L of DCP in one of 10 samples from Lake Superior near a pulp and paper discharge at Thunder Bay. In the same study, no DCP was detected in 11 water samples from the St. Mary's River near a pulp and paper mill.

Information on the occurrence of DCP's in chlorinated municipal wastewater is conflicting. Barnhart and Campbell (1972) concluded that sewage chlorination results in a mixture of chlorophenols. Lee and Morris (1972) reported the formation of 2,4-DCP in laboratory solutions of chlorine and phenol at various pH levels. Burttschell et al. (1959) felt that 2,4- and 2,6-DCP should be formed by chlorination of phenol in water. Jolley et al. (1978) examined CP formation under conditions simulating chlorination of sewage

effluents and power plant cooling water, but found no DCP's. Glaze *et al.* (1978) found no DCP in superchlorinated municipal wastewaters. On the basis of these studies, one may conclude that chlorinated municipal sewage is probably not a significant source of DCP's.

Industrial and municipal landfill sites may also be significant sources of DCP to aquatic environments. Elder *et al.* (1981) identified DCP's in waters draining dump sites in Niagara Falls, New York. Garrett (1980) reported DCP's in leachates from landfill sites in Greater Vancouver.

Incineration of municipal garbage may introduce DCP to the atmosphere. Olie *et al.* (1977) studied the occurrence of organic pollutants in flue gas condensates and reported that the most abundant chlorinated organics are the di-, tri- and tetra-CP's. DCP released to the atmosphere may reach surface waters through fallout processes.

3.2 Environmental Fate

3.2.1 Physical and Chemical Properties

A summary of the physicochemical properties of selected DCP's is given in Table 3-2. These properties control the behaviour of DCP's in surface water environments.

3.2.2 Photolysis

A few studies have examined the photodegradation of 2,4-DCP. These have generally been investigations of *in vitro* processes. 2,4-DCP formed in soil from the photolysis of phenoxyacetate herbicides (eg. 2,4-D, Nitrofen) degrades further to catechol intermediates and finally to succinic acid (Kearney and Kaufman 1972). This photodecomposition sequence may also occur to some extent in natural surface waters. Crosby and Tutass (1966) reported the photodegradation of 2,4-DCP under near ultraviolet and solar radiation conditions. After 10 days of solar irradiation, all of the 2,4-DCP was converted to an acidic, dark tarry substance formed from polymerization of breakdown products. Plimmer and Klingebiel (1971) reported negligible photolysis of 2,4-DCP at wavelengths above 280 nm and a requirement for a photosensitizer such as riboflavin before photolysis would occur in any situation. In a study of microbial

degradation of 2,4-DCP in natural lake water, Aly and Faust (1964) reported that photolysis occurred at an insignificant rate in comparison with microbial catabolism. On the basis of this study, the U.S. EPA (1979) concluded that photolysis is probably insignificant in natural surface waters.

3.2.3 Microbial Degradation

The microbial degradation of 2,4-DCP has been studied considerably, particularly in connection with work on the herbicide 2,4-D. In silt suspensions, 2,4-DCP was degraded completely in 5 to 9 days at initial concentrations of 50 mg/L. (Alexander and Aleem 1961). Pitter (1976) observed 98% degradation of 2,4-DCP by activated sludge bacteria adapted for 20 days. Tyler and Finn (1974) studied the growth kinetics of a pseudomonad culture on 2,4-DCP. The highest growth rate was 0.12/h at 25°C and pH 7.1-7.8. Growth was inhibited at 2,4-DCP concentrations of 25 mg/L. The rate of bacterial growth (and thus 2,4-DCP breakdown) was dependent on concentration and on prior adaptation of the culture organisms. Aly and Faust (1964) examined the disappearance of 2,4-DCP from samples of aerated lake water (pH 7, 25°C) in the laboratory. DCP in solution at 100 ug/L was completely eliminated in 9 days while levels of 500 and 1,000 ug/L were 97.5% eliminated in 30 days. A half-life of 6 days for 2,4-DCP was determined. Unfortunately, volatilization of 2,4-DCP was not controlled and may have accounted for some of this disappearance. Under simulated eutrophic low oxygen conditions, Aly and Faust (1964) reported greater persistence, with considerable levels of 2,4-DCP remaining after 43 days. In a freshwater nutrient medium, Kreuk and Hanstveit (1981) measured 70% biodegradation of 2,6-DCP in 80 days. Chu and Kirsch (1972) found that an unidentified bacillus in soil culture could degrade 67% of added 2,4-DCP in 150 minutes. Pseudomonas, Achromobacter, Arthrobacter, Flavobacterium and mixed soil bacteria cultures have all been shown to metabolize 2,4-DCP (Alexander and Aleem 1961; Macrae et al. 1963; Ingols et al. 1966; Loos et al. 1967; Bollag et al. 1968; Tiedje et al. 1969; Paris and Lewis 1973).

Data on conditions needed for induction of DCP breakdown by mixed cultures of microbes are sparse. Also, information on minimum levels of DCP required for induction of bacterial catabolism is unavailable. The U.S. EPA (1979) felt that concentrations of DCP needed to initiate biodegradation would probably be reached only near discharges. Degradation should be relatively rapid in stagnant or slow-flowing receiving waters with

high levels of DCP, provided dissolved oxygen levels are adequate. In fast-flowing receiving waters, microflora will probably be poorly adapted for degradation of DCP and the rate of biodegradation should be relatively slow.

3.2.4 Chemical Degradation

Aly and Faust (1964) reported the decomposition of 2,4-DCP in buffered, biologically active lake water. At pH 7 and 25°C, and at initial concentrations of 100, 500 and 1,000 ug/L, 50% of the compound was decomposed in six days. In simulated anaerobic, eutrophic conditions, 2,4-DCP persisted for over 43 days. However, Aly and Faust (1964) felt that biological activity and not simple chemical degradation was responsible for the observed results.

Morrison and Boyd (1973) inferred that 2,4-DCP should undergo oxidation reactions where hydroxyl radicals attack C-2 and C-4 positions resulting in complex mixtures. However, the relative importance of this reaction in the environment is unknown. NRCC (1982) suggested that oxidation of CP's in the environment requires further study.

Hydrolysis of 2,4-DCP is probably insignificant in the environment. The covalent bond of a substituent attached to an aromatic ring is usually resistant to hydrolysis because of a high negative charge density around the aromatic nucleus (Morrison and Boyd 1973).

The U.S. EPA (1979) concluded that chemical degradation processes are probably not important in controlling the fate of 2,4-DCP in aquatic environments.

3.2.5 Sorption Processes

Published log octanol-water distribution coefficients (log P) for 2,4-DCP are 2.75 (U.S. EPA 1979) and 3.08 (Hansch and Leo 1979). The log P value for 2,6-DCP was given as 2.84 by Hansch and Leo (1979). Based on log P sediment sorption characteristics described by Karickhoff et al. (1979), a slight affinity of DCP's for organic materials in sediments and particulates is indicated. In sediment and water samples from the Rhine River mouth area, Wegman and Broek (1983) reported sediment enrichment factors of 440 times for 2,4-DCP and 20 times for 2,6-DCP. Sediment concentrations were expressed in ug/kg dry weight. Concentrations of 2,3-, 2,5-, 3,4- and 3,5-DCP in

sediment were also reported but enrichment factors were not given. Information on sediment quality (grain size, organic content) was not given. Also, the authors do not state whether water samples were filtered or centrifiged before analysis.

The only specific study of DCP adsorption by soils was undertaken by Aly and Faust (1964). Sorption to kaolinite, bentonite (a montmorillonitic clay) and illite clays was measured. The order of decreasing sorption was bentonite > illite > kaolinite and was correlated with specific surface area. From the results of this study, the U.S. EPA (1979) concluded that suspended or sedimentary clays will not remove significant amounts of 2,4-DCP from solution in natural waters.

3.2.6 Volatilization

Compounds with moderate solubilities and low vapour pressures such as 2,4-DCP do not readily volatilize from water (U.S. EPA 1979). Also, 2,4-DCP is a weak acid ($pK_a=7.85$; Pearce and Simkins 1968) and will be about 50% ionized and solvated in surface waters. Kirk and Othmer (1964) stated that 2,4-DCP is not volatile from aqueous alkaline solutions. On the basis of this information, volatilization is not considered significant in the environmental transport of 2,4-DCP.

Specific information on the importance of volatilization in other DCP's has not been provided in the literature. Because these compounds dissociate, are weakly acidic and are slightly soluble in water (Table 3-1), the role of volatilization in their removal from water is probably similar to that in 2,4-DCP.

3.2.7 Bioaccumulation

Little information exists in the accumulation of DCP's in aquatic biota (Table 3-2). Saarikoski and Viluksela (1982) exposed guppies to sublethal concentrations of 2,6-DCP at pH 6 and 26°C. Steady-state bioconcentration was reached within 24 hours. A bioconcentration factor of 12X relative to water was measured. The same theoretical bioconcentration factor was calculated using a log octanol-water partition coefficient - log bioconcentration factor correlation. Bacon (1978) reported 2,4-DCP in various marine biota near a pulp mill discharge in St. John, N.B., although no CP's were observed in water samples. Clams and shrimp were contaminated, but tissue concentrations were

not given. Winter flounder, shad, gaspereau, rainbow smelt, sturgeon and tomcod were all reported contaminated with 2,4-DCP. The highest concentration (9 ug/g lipid) was observed in smelt. With log P values of 2.75 (U.S. EPA 1979) to 3.08 (Hansch and Leo 1979) (mean=2.92) for 2,4-DCP and 2.84 for 2,6-DCP, Hansch and Leo (1979) calculated bioconcentration factors for fish range from 33 to 67 with respect to concentrations dissolved in water (Neely et al. 1974; Veith et al. 1979; Mackay 1982).

Assuming the mean BCF of 65 for 2,4-DCP (Table 3-2) and using Neely's (1979) model, an uptake rate constant of 2.1 (k_1) and a fractional clearance rate of 0.032 h^{-1} for 2,4-DCP are calculated. This rate of clearance is relatively rapid, and is equivalent to a residence time of 31 h. While a constant rate of clearance is calculated, tissue depuration rates may decrease at very low tissue concentrations.

One study has examined biological uptake of 2,4-DCP in plants. Isensee and Jones (1979) reported bioconcentration factors of 9.2X and 0.65X for oats and soybean, respectively, from dilute solutions (0.2 mg/L).

3.2.8 Probable Fate

Dichlorophenols are readily biodegraded in the environment. Bioaccumulation factors are relatively low and clearance rates in fish are high. These compounds have some tendency to accumulate on particulate materials and sedimentation of suspended solids having high organic levels may be an important removal process in some instances. Photolysis, chemical degradation and volatilization are probably not important processes for removal from surface waters. Table 3-3 summarizes the aquatic fate of 2,4-DCP. The overall environmental half-life is estimated at ≥ 6 days, based on biodegradation processes.

3.3 Distribution in Ontario

Information on environmental levels of DCP's in Ontario is sparse. Of 10 water samples from Thunder Bay near a pulp and paper mill discharge, one sample had 4 ug/L of DCP (Robinson and Smillie 1977). No DCP's were found in 11 samples from the St. Mary's River near a pulp and paper discharge at Sault Ste. Marie. Because of the potential diversity of sources of DCP's, particularly the 2,4-DCP isomer, the occurrence of these

compounds in Ontario may be widespread. However, because of relatively rapid rates of biodegradation, DCP's are likely more common near source discharges than throughout watersheds and basins.

3.4 Effects on Aquatic Organisms

For five of the six DCP isomers, useful data on biological effects are available. Most of this information pertains to the 2,4-DCP isomer which is widely used as an intermediate compound in the chemical industry. The DCP isomers are somewhat more toxic than the MCP's, again reflecting the relationship between toxicity and the degree of chlorination. The majority of toxicity levels recorded for the DCP group were obtained from static bioassays in which contaminant concentrations were calculated rather than measured. The DCP group, particularly the 2,4-DCP isomer, has been shown to cause fish flavour impairment.

Relevant data on acute and chronic effects of DCP on aquatic life are given in Tables 3-4 to 3-9. The information is summarized in Figure 3-1 and compared to the various existing regulatory standards.

3.4.1 Acute Toxicity

A listing of the acute toxicity data examined for this review is provided in Tables 3-4 and 3-5. A considerable amount of high quality data has been gathered for 2,4-DCP. Approximately one-half of the studies that generated these data consisted of flow-through bioassays on fish and invertebrates where contaminant concentrations were measured in the test vessels. The acute 96-hour LC_{50} values ranged from 1,240 ug/L for goldfish embryos (Birge et al. 1979) to 8,300 ug/L for fathead minnow (Phipps et al. 1981). Acute, 4-day tests on channel catfish embryos showed LC_{50} values of 1,770 ug/L (Birge et al. 1979). Adult bluegills showed LC_{50} values of 2,020 ug/L (Buccafusco et al. 1981) and rainbow trout had LC_{50} values of 2,800 ug/L (PPRIC 1979). A 24-hour LC_{50} conducted on brown trout showed toxicity levels of 1,700 ug/L (Hattula et al. 1981). From the data listed in Tables 3-4 and 3-5, it would appear that sensitive invertebrates and fish respond to 2,4-DCP at similar levels (Kopperman et al. 1974).

Although some acute toxicity testing has been carried out with 2,6- and 3,4-DCP isomers (Applegate et al. 1957), these bioassays were of short duration and of questionable control. Hattula et al. (1981) did find a 24-hour LC₅₀ value of 4,000 ug/L for 3,6-DCP.

3.4.2 Chronic Toxicity

No information was found on the chronic effects of any of the DCP isomers, with the exception of 2,4-DCP. These data are provided in Tables 3-6 and 3-7. Holcombe et al. (1982) conducted 32-day early life stage bioassays on fathead minnows and found chronic effects at minimum levels of 375 ug/L. In this study, embryos were more resistant to 2,4-DCP than larval or early juvenile stages. Fathead embryos were unaffected at concentrations as high as 1,240 ug/L. Similar studies by Birge et al. (1979) indicated that rainbow trout embryo and larval stages had comparable sensitivities.

Investigations on the influence of pH on 2,4-DCP toxicity were carried out by Holcombe et al. (1980). Toxicity decreased with increasing pH as was the case with MCP isomers, reflecting the fact that 2,4-DCP is more toxic in its dissociated form. Birge et al. (1979) also carried out eight-day embryo-larval exposures at various hardnesses and found that hardness had little effect on toxicity.

3.4.3 Plant Toxicity

The toxicity of DCP to aquatic plants has been investigated to a limited degree, and only for 2,4-DCP (Table 3-8). Huang and Gloyna (1968) studied the toxic effects of 2,4-DCP on Chlorella pyrenoidosa. There was a 50% reduction in photosynthetic activity at a concentration of 50 mg/L. Complete destruction of chlorophyll occurred at 100 mg/L. Similarly, a 50% reduction of chlorophyll was observed by Blackman et al. (1955) for duckweed (Lemna minor) exposed to 58 mg/L 2,4-DCP.

3.4.4 Flavour Impairment

Substantial work has been carried out on the potential for fish tainting by 2,4-DCP, 2,3-DCP, 2,5-DCP and 2,6-DCP (Shumway and Palensky 1973). The data in Table 3-9 suggest that tainting concentrations of DCP are one to three orders of magnitude lower than those causing acute mortality. Thresholds for flavour impairment varied from 84 ug/L for 2,3-DCP to 1 ug/L for 2,4-DCP in rainbow trout.

Shumway and Palensky (1973) also investigated the rate of 2,4-DCP clearance by exposing contaminated fish to clean water. Flavour impairment was substantially reduced after 6.5 hours in trout which had been exposed to 100 ug/L 2,4-DCP. After 33.5 hours, flavour was normal. The authors concluded that flavour impairment from DCP is acquired more rapidly than it is lost. Relatively rapid rates of uptake and clearance of off-flavour are consistent with data on bioaccumulation of DCP's (Section 3.2.7). Tainting, therefore, appears to be the most sensitive response affecting resource use.

3.4.5 Criteria Development

The U.S. EPA (1980a, c) derived criteria for the protection of aquatic life by means of two approaches. The first was a maximum 'not-to-exceed' level based on acute toxicity data, and the second was a 24-hour average level based on chronic toxicity data. At the time of the U.S. EPA review, insufficient information was available for the development of criteria for all DCP isomers. However, acute maximum and chronic 24-hour average criteria were established for 2,4-DCP. More recent information (Birge et al. 1979) would suggest a maximum acute criterion of 1,480 ug/L.

Use of the standard application factor of 0.05 for non-persistent compounds, times the lowest acute value of 1,480 ug/L as outlined in Section 1.4, would result in a criterion of about 75 ug/L. However, this value is unsuitable because the lowest chronic effect value is 70 ug/L. Tainting threshold values lie even below this level.

The 2,4-DCP isomer is the most critical in terms of flavour impairment, with a tainting threshold as low as 0.4 ug/L (Table 3-9). It is recommended that the objective for dichlorophenols be set at 0.2 ug/L (one-half of the lowest tainting threshold; see Section 1.4) to protect against tainting and toxicity in all aquatic organisms.

TABLE 3-1: PHYSICAL PROPERTIES OF SELECTED DICHLOROPHENOLS
(adapted from Jones 1981)

CAS No.	Compound	Commercial utility	Formula	Molecular Weight	Boiling point ^a (760 mm or as stated), °C	Melting point ^a (°C)	Dissociation constant ^b at 25°C, K _a
576249	2,3-DCP	No	"	163.00	206 ^b	57-59	3.6x10 ⁻⁷
120832	2,4-DCP	Yes	C ₆ H ₄ Cl ₂ O	"	210	45	2.1x10 ⁻⁸
583788	2,5-DCP	No	"	"	211(744)	59	4.5x10 ⁻⁷
87650	2,6-DCP	No	"	"	219-220(740)	68-69	1.6x10 ⁻⁷
95772	3,4-DCP	No	"	"	253.5(767)	68	4.1x10 ⁻⁸
591355	3,5-DCP	No	"	"	233(757)	68	1.2x10 ⁻⁷
2,3-DCP	7.70	-	-	-	-	-	-
2,4-DCP	7.85	7.85	3.8x10 ⁻²	1.383 ⁶⁰ /25	1 mm@76.5C ^g	2.75 ⁱ	62Colorless
needles, or			(45 mg/L@20°C) ^h		1 mm@53C ^h	3.08 ^j	yellow solid
2,5-DCP	7.51	-	slightly ^a	-	-	-	-
2,6-DCP	6.79	6.91	-	-	1 mm@59°C ^h	2.84 ^j	-
3,4-DCP	8.59	-	slightly ^a	-	-	-	-
3,5-DCP	8.19	slightly ^a	-	-	-	-	-

^a Weast (1974, 1978)

^b Doedens (1967)

^c Pearce and Simpkins (1968)

^d Farquharson et al (1958)

^e Blackman et al (1955); 2,4-DCP is moderately soluble at neutral pH and highly soluble in alkaline solutions because it readily dissociates to form the alkaline salt.

^f Density is relative to water, the superscript indicates the temperature of the liquid and the subscript the temperature of the water to which the density is referred.

^g Sax (1975)

^h Kingsbury et al. (1979)

ⁱ U.S. EPA (1979)

^j Hansch and Leo (1979)

TABLE 3-2: BIOCONCENTRATION FACTORS AND DEPURATION RATES FOR
DICHLOROPHENOLS IN FRESHWATER BIOTA

	BCF	Depuration	Reference
<u>2,6-DCP</u>			
<u>Poecilia reticulata</u>	12	-	1
Fish (calculated)	33	-	2
	52	-	3
	61	-	4
<u>2,4-DCP</u>			
Fish (calculated)	* 39	-	2
	* 60	-	3
	* 67	clearance rate = 0.032 h^{-1}	4,5

* based on a mean Log P of 2.92

1 Saarikoski and Viluksela (1982)

2 Mackay (1982)

3 Veith et al. (1979)

4 Neely et al. (1974)

5 Neely (1979) (see text for assumptions)

TABLE 3-3: SUMMARY OF AQUATIC FATE OF 2,4-DICHLOROPHENOL
(after U.S. EPA 1979)

Environmental Process	Summary Statement	Rate	Half Life	U.S. EPA's Confidence of Data
<u>Degradation Processes</u>				
Photolysis	- probably insignificant in natural waters.	-	-	low
*Biodegradation	- a well-substantiated process; rate depends on water quality and adaptation of bacteria.	-	about 6 days, longer in anaerobic water	medium
Chemical Degradation	- oxidation and hydrolysis reactions are probably insignificant.	-	-	low
<u>Transport Processes</u>				
*Sorption	- may be of some importance in organic particulates based on a log P of 2.75-3.08; sediment accumulation of various DCP's observed in Rhine River sediments.	-	-	medium
Volatilization	- not considered important in natural surface waters.	-	-	medium
Bioaccumulation	- reported in marine biota and crop plants; calculated BCF = 39 to 67 based on log P of 2.92	-	- residence time in 500 g rainbow trout about 31 h.	medium
Probable overall environmental half-life ≥ 6 days				

*Probable dominant processes in degradation and removal.

TABLE 3-4: PRIMARY ACUTE TOXICITY DATA FOR THE DICHLOROPHENOLS

Isomer Evaluated	Species	Method ¹	Individual Results (ug/L)	Test Laboratory Water Quality				Laboratory	Reference
				Geometric Mean (ug/L)	Mean pH	Mean Temp. (°C)	Hardness (as CaCO ₃ mg/L)		
2,4-DCP	Cladoceran <u>Daphnia magna</u>	48hr-LC ₅₀ , S,U	2,610		-	-	-	-	Kopperman et al. 1974
			2,600	2,605	8.0	22	173	E,G&G Bionomics, Mass.	LeBlanc 1980
	Fathead Minnow <u>Pimephales promelas</u>	96hr-LC ₅₀ , FT,M	8,230		7.5	23	45	U.S. EPA Env. Research Lab. Duluth, Minn.	Phipps et al. 1981 ³
			8,300	8,260	7.5	23	45		
	Rainbow Trout <u>Salmo gairdneri</u>	96hr-LC ₅₀ , S,U	2,800	2,800	7.7	12	280	Pulp & Paper Res. Inst. Pt. Claire, Que.	PPRIC 1979
	Bluegill <u>Lepomis macrochirus</u>	96hr-LC ₅₀ , S,U	2,020	2,020	7.2	22	40	E,G&G Bionomics, Mass.	Buccafusco et al. 1981 ^{2,3}
	Goldfish <u>Carassius auratus</u>	96hr-LC ₅₀ , FT,M	1,760		7.8	22	50	-	Birge et al. 1979
		embryo exposure	1,240	1,480	7.8	22	200	-	
	Channel Catfish <u>Ictalurus punctatus</u>	96hr-LC ₅₀ , FT,M	1,850	-	7.8	22	50	-	Birge et al. 1979
		Embryo exposure	1,700	1,770	7.8	22	200	-	

¹Terms: FT = flow-through bioassay, Semi S.= Static bioassay with solution replacement, S = static bioassay, U = test tank concentrations unmeasured, M = test tank concentrations measured, SW = water of low hardness
MW = water of medium hardness, HW = water of high hardness

²Conductivity reported

³Alkalinity reported

⁴Major ions reported

TABLE 3-5: SECONDARY ACUTE TOXICITY DATA FOR THE DICHLOROPHENOLS

Isomer Evaluated	Species	Method	Results (ug/L)	Test Laboratory Water Quality			Laboratory	Reference
				Mean pH	Mean Temp. (°C)	Mean Hardness (as CaCO ₃ mg/L)		
2,4-DCP	Crayfish <u>Orconectes propinquus</u>	48 hr-LC ₁₀₀ ,S,U	10,000	-	19	-	Dept. of Zoology Univ. of Toronto, Ontario	Telford 1974
	Lymnaeid Snail	24 hr-LC ₁₀₀ ,S,U	10,000	-	-	-	Florida Agric. Exper. Stn., Florida	Batte & Swanson 1952
	Bluegill <u>Lepomis macrochirus</u>	12 hr-LC ₁₀₀ ,S,U	5,000	-	12.8	-	U.S. Fish & Wild. Serv., Ann Arbor, Michigan	Applegate <u>et al.</u> 1957
	Rainbow Trout <u>Salmo gairdneri</u>	3 hr-LC ₁₀₀ ,S,U	5,000	-	12.8	-	"	"
	Goldfish <u>Carassius auratus</u>	24 hr-LC ₅₀ ,S,U	7,800	-	-	-	-	Kobayashi <u>et al.</u> 1979
	Brown Trout <u>Salmo trutta</u>	24 hr-LC ₅₀ ,S,U	1,700	-	5	-	Dept. of Cell Biology, Univ. of Jyvaskyla, Finland	Hattula <u>et al.</u> 1981
	Sea Lamprey <u>Petromyzon marinus</u>	12 hr-LC ₁₀₀ ,S,U	5,000	-	12.8	-	U.S. Fish & Wild. Serv., Ann Arbor, Michigan	Applegate <u>et al.</u> 1957

TABLE 3-5: SECONDARY ACUTE TOXICITY DATA FOR THE DICHLOROPHENOLS (Cont'd)

Isomer Evaluated	Species	Method	Results (ug/L)	Test Laboratory Water Quality			Laboratory	Reference
				Mean pH	Mean Temp. (°C)	Mean Hardness (as CaCO ₃ mg/L)		
2,6-DCP	<u>Northern Squawfish</u> <u>Ptychocheilus oregonensis</u>	3 hr-LC ₁₀₀ ,S,U	10,000	-	10.6	-	Forest, Wild. & Range Exp. Stn. Univ. of Idaho	MacPhee & Ruelle 1969
	<u>Coho Salmon</u> <u>Oncorhynchus kisutch</u>	1 hr-LC ₁₀₀ ,S,U	10,000	-	10.6	-	"	"
	<u>Chinook Salmon</u> <u>Oncorhynchus tshawytscha</u>	1 hr-LC ₁₀₀ ,S,U	10,000	-	10.6	-	"	"
	<u>Rainbow Trout</u> <u>Salmo gairdneri</u>	13 hr-LC ₁₀₀ ,S,U	5,000	-	12.8	-	U.S. Fish & Wild. Serv., Ann Arbor Michigan	Applegate <u>et al.</u> 1957
	<u>Bluegill</u> <u>Lepomis macrochirus</u>	5 hr-LC ₁₀₀ ,S,U	5,000	-	17.0	-	"	"
	<u>Brown Trout</u> <u>Salmo trutta</u>	24 hr-LC ₅₀ ,S,U	4,000	-	5	-	Dept. of Cell Biology, Univ. of Jyväskylä, Finland	Hattula <u>et al.</u> 1981

TABLE 3-5: SECONDARY ACUTE TOXICITY DATA FOR THE DICHLOROPHENOLS (Cont'd)

Isomer Evaluated	Species	Method	Results (ug/L)	Test Laboratory Water Quality			Laboratory	Reference
				Mean pH	Mean Temp. (°C)	Mean Hardness (as CaCO ₃ mg/L)		
3,4-DCP	Rainbow Trout <u>Salmo gairdneri</u>	3 hr-LC ₁₀₀ ,S,U	5,000	-	12.8	-	U.S. Fish & Wild. Serv., Ann Arbor Michigan	Applegate <u>et al.</u> 1957
	Bluegill <u>Lepomis macrochirus</u>	3 hr-LC ₁₀₀ ,S,U	5,000	-	17.0	-	"	"
	Sea Lamprey <u>Petromyzon marinus</u>	11 hr-LC ₁₀₀ ,S,U	5,000	-	-	-	"	"

¹Terms: S = Static bioassay, U = test tank concentrations unmeasured

TABLE 3-6: PRIMARY CHRONIC TOXICITY DATA FOR THE DICHLOROPHENOLS

Isomer Evaluated	Species	Method ¹	Test Conc. Ranges (ug/L)	Test Laboratory Water Quality				Laboratory	Reference
				Conc. of Lowest Chronic Effect (ug/L)	Mean pH	Mean Temp. (°C)	Hardness (as CaCO ₃ mg/L)		
2,4-DCP	<u>Fathead Minnow Pimephales promelas</u>	32 day-Early, Life Stage, FT,M	290-460	375	7.5	25	46	U.S EPA Env. Res. Lab Duluth, Minn.	Holcombe, <u>et al.</u> 1982 ³
		23 day-LC ₅₀ Embryo exposure FT, M	-	80	7.8	14	50	-	Birge <u>et al.</u> 1979
	<u>Rainbow Trout Salmo gairdneri</u>			70	7.8	14	200	-	
		27 day-LC ₅₀ Embryo-larval exposure FT,M	-	80	7.8	14	50	-	Birge <u>et al.</u> 1979
				70	7.8	14	200	-	
								-	

¹Terms: FT = flow-through bioassay, Semi S.= Static bioassay with solution replacement, S = static bioassay, U = test tank concentrations unmeasured, M = test tank concentrations measured, SW = water of low hardness MW = water of medium hardness, HW = water of high hardness

²Conductivity reported

³Alkalinity reported

TABLE 3-7: SECONDARY CHRONIC TOXICITY DATA FOR THE DICHLOROPHENOLS

Isomer Evaluated	Species	Method ¹	Results (ug/L)	Test Laboratory Water Quality			Laboratory	Reference
				Mean pH	Mean Temp. (°C)	Hardness (as CaCO ₃ mg/L)		
2,4-DCP	Crayfish <u>Orconectes propinquus</u>	10 day-LC ₁₄ , S,U Increased blood glucose levels	1,000	-	19	-	Dept. of Zoology Univ. of Toronto Ontario	Telford 1974
	<u>Orconectes immunis</u>	7 day-LC ₁₀₀ , S,U	5,000	-	19	-	Dept. of Zoology Univ. of Toronto Ontario	Telford 1974
		10 day increased blood glucose levels	1,000	-	19	-		
	<u>Cambarus robustus</u>	7 day-LC ₁₀₀ , S,U	5,000	-	19	-	Dept. of Zoology Univ. of Toronto Ontario	Telford 1974
		10 day increased blood glucose levels	1,000	-	19	-		
	<u>Fathead Minnow</u> <u>Pimephales promelas</u>	8 day-LC ₅₀ , Ft,M	6,500	7.5	23	45	U.S. EPA Env. Res. Lab Duluth, Minn.	Phipps et al. 1981
		3 day-LC ₅₀ , FT,M	6,500	7.5	23	45		
		8 day-LC ₇₂ , FT,M	7,400	7.4	25	46	U.S. EPA Env. Res. Lab Duluth, Minn.	Holcombe et al. 1980
		8 day, FT, M No Mortality	7,400	9.1	25	46		

TABLE 3-7: SECONDARY CHRONIC TOXICITY DATA FOR THE DICHLOROPHENOLS

Isomer Evaluated	Species	Method ¹	Results (ug/L)	Test Laboratory Water Quality			Laboratory	Reference
				Mean pH	Mean Temp. (°C)	Hardness (as CaCO ₃ mg/L)		
2,4-DCP	Channel Catfish <u>Ictalurus punctatus</u>	8 day-LC ₅₀ , embryo and larval exposure	1,350 1,070	- -	- -	50 200	- -	Birge <u>et al.</u> 1979
	Goldfish <u>Carassius auratus</u>	8 day-LC ₅₀ , embryo and larval exposure	390 260	- -	- -	50 200	- -	

¹Terms: FT = flow-through bioassay, Semi S.= Static bioassay with solution replacement, S = static bioassay,
U = test tank concentrations unmeasured, M = test tank concentrations measured, SW = water of low hardness
MW = water of medium hardness, HW = water of high hardness

²Conductivity reported

³Alkalinity reported

TABLE 3-8: PLANT VALUES FOR DICHLOROPHENOLS

Isomer Evaluated	Species	Method	Results (ug/L)	Test Laboratory Water Quality			Laboratory	Reference
				Mean pH	Mean Temp. (°C)	Mean Hardness (as CaCO ₃ mg/L)		
2,4-DCP	Alga <u>Chlorella pyrenoidosa</u>	Complete destruction of chlorophyll	100,000	7.0	25	-	Civil Eng. Dept., Univ. of Texas	Huang & Gloyna 1968
	Alga <u>Chlorella pyrenoidosa</u>	56.4% reduction of photosynthetic oxygen production	50,000	7.0	25	-	"	"
	Duckweed <u>Lemna minor</u>	50% reduction in chlorophyll	58,320	5.1	25	-	Dept. of Agric., Oxford Univ., England	Blackman <u>et al.</u> 1955

TABLE 3-9: FISH TAINTING VALUES FOR THE DICHLOROPHENOLS

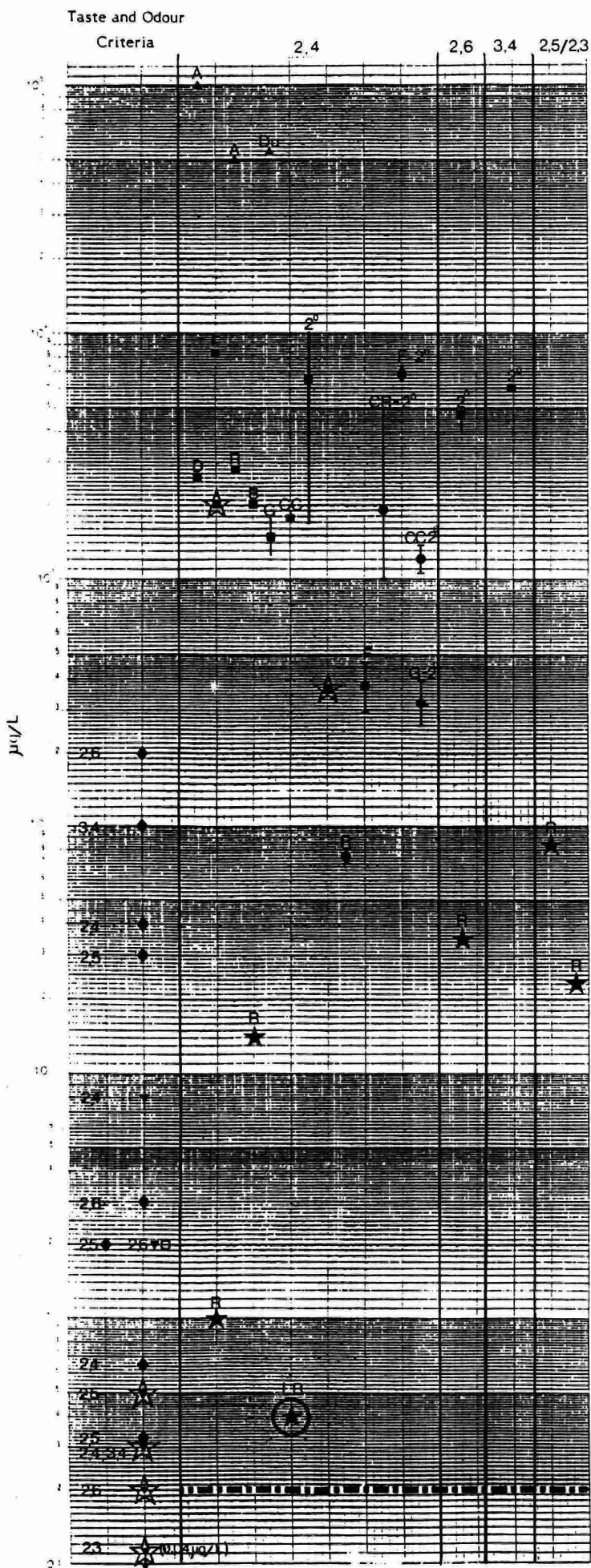
Isomer Evaluated	Species	Method ¹	Test Laboratory Water Quality				Laboratory	Reference
			Estimated Flavour Impairment Threshold Conc. (ug/L)	Mean pH	Mean Temp. (°C)	Hardness (as CaCO ₃ mg/L)		
2,3-DCP	Rainbow Trout <u>Salmo gairdneri</u>	ETC, FT, U	84	7.5	15	SW	Oak Creek Fish. Lab., Oregon Univ., Corvallis	Shumway & Palensky 1973 ^{2,4}
2,4-DCP	Rainbow Trout <u>Salmo gairdneri</u>	ETC, FT, U	1	7.5	15	SW	"	"
	Bluegill <u>Lepomis macrochirus</u>	ETC, FT, U	14	7.5	15	SW	"	"
	Largemouth Bass <u>Micropterus salmoides</u>	ETC, FT, U	0.4	7.5	15	SW	"	"
2,5-DCP	Rainbow Trout <u>Salmo gairdneri</u>	ETC, FT, U	23	7.5	15	SW	"	"
2,6-DCP	Rainbow Trout <u>Salmo gairdneri</u>	ETC, FT, U	35	7.5	15	SW	"	"

¹Terms: FT = flow-through bioassay, Semi S.= Static bioassay with solution replacement, S = static bioassay, U = test tank concentrations unmeasured, M = test tank concentrations measured, SW = water of low hardness, MW = water of medium hardness, HW = water of high hardness

²Conductivity reported

³Alkalinity reported

⁴Major ions reported



CODES

- ◆ Odour Threshold
- ▼ Taste Threshold
- Acute Toxicity
- Chronic Toxicity
- ▲ Plant Data
- ★ Tainting (Fish Flesh)
- ☆ EPA Criteria
- Soviet Criteria
- 2° Secondary Data
- Recommended Criterion
- Vertical bars represent data ranges
- Critical Value in Criteria Selection

Test Species

- Du Duckweed
- A Alga
- D Daphnia
- F Fathead Minnow
- B Bluegill
- G Goldfish
- R Rainbow Trout
- Gu Guppy
- C Carp
- LB Largemouth Bass

FIGURE 3-1:
DICHLOROPHENOLS
TOXICITY AND CRITERIA SUMMARY

Recommended Criterion 0.2 µg/L

4.0 TRICHLOROPHENOLS

There are six potential isomers of trichlorophenol (TCP):

2,3,4-trichlorophenol	(2,3,4-TCP)
2,3,5-trichlorophenol	(2,3,5-TCP)
2,3,6-trichlorophenol	(2,3,6-TCP)
2,4,5-trichlorophenol	(2,4,5-TCP)
2,4,6-trichlorophenol	(2,4,6-TCP)
3,4,5-trichlorophenol	(3,4,5-TCP)

4.1 Occurrence

Of six isomers of trichlorophenol (TCP), only 2,4,5-TCP and 2,4,6-TCP have commercial utility (Jones 1981). Correspondingly, most available information on TCP's specifically concerns these isomers. Neither are manufactured in Canada. Canadian distributors include:

Atlantic Trading Company 3335 Yonge St., Suite 404 Toronto, Ontario M4N 2M2	2,4,5-TCP
---	-----------

Bayer (Canada) Ltd. through Dow Chemical of Canada Ltd. P.O. Box 1012, Highway #40 Sarnia, Ontario N7T 7K1	2,4,5-TCP 2,4,6-TCP
---	------------------------

Record Chemical Co., Inc. 840 Montee de Liesse Montreal, Quebec H4T 1N8	2,4,5-TCP
---	-----------

Tennant Charles and Co. (Canada) Ltd. 34 Clayson Rd. Weston, Ontario M9M 2G8	2,4,6-TCP
--	-----------

In the U.S. 2,4,5-TCP is used in the production of the insecticide Ronnel and the herbicides 2,4,5-trichlorophenoxyacetic acid (2,4,5-T), Silvex and Erbon. Both the TCP's and tetrachlorophenols are used as wood preservatives when in combination with other compounds (notably pentachlorophenol). The 2,4,5-TCP isomer is also used in the production of hexachlorophene used in disinfectants and sanitation products for domestic, hospital and veterinary use.

Biocides containing 2,4,5-TCP may contain 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD), a highly toxic and carcinogenic substance (U.S. EPA 1980a). Thus, 2,4,5-TCP formed from degradation of 2,4,5-T in the environment may be accompanied by TCDD. The environmental behaviour and toxicity of TCDD will not be discussed in this report.

The TCP's occur in wastes from wood preserving and pulp and paper industries. Garrett (1980) reported several isomers in discharges from forest products industries in Greater Vancouver. Bacon (1978) reported 2,4,6-TCP in Kraft mill effluent at St. John, N.B. Robinson and Smillie (1977) observed 3 and 23 ug/L of TCP in two of 10 surface water samples taken in Thunder Bay near a pulp and paper mill discharge. Environment Canada (1979a) reported 2,4,6-TCP in laboratory prepared bleach effluents from various softwood and hardwood pulping processes.

TCP's may form in water and sewage by the chlorination of phenol. Garrett (1980) observed several TCP isomers in Greater Vancouver municipal sewage influents and effluents. Burttschell *et al.* (1959) proposed that 2,4,6-TCP forms 40-50% of the chlorophenols produced by chlorination of water containing phenol.

TCP's may be produced as degradation products in agricultural systems. Degradation of Lindane in soil results in the formation of 2,3,4-, 2,3,5- and 2,4,5-TCP (Engst *et al.* 1977). The 2,4,5 isomer may form from photolysis of 2,4,5-T, as observed in aerated water by Crosby and Wong (1973). The metabolic breakdown products of several herbicides in livestock include 2,4,5-TCP (U.S. EPA 1980a). Thus runoff and erosion in farmland may introduce TCP to surface water systems.

Wastes from chemical industries may also contain TCP's. Elder *et al.* (1981) observed TCP in surface waters draining industrial landfill sites in Niagara Falls, New York. Garrett (1980) reported TCP at concentrations of up to 2,400 ug/L and 3,120 ug/L for 2,4,5- and 2,4,6-TCP in various industrial and municipal wastes in Greater Vancouver.

Incineration of municipal refuse may provide a minor source of TCP's to surface waters. Olie et al. (1977) reported TCP's in flue gas from municipal incinerators. Fallout of TCP from the atmosphere may result in entry to aquatic environments.

4.2 Environmental Fate

4.2.1 Physical and Chemical Properties

A summary of the physicochemical properties of selected TCP's, as provided by Jones (1981), is presented in Table 4-1. These properties will control the behaviour of TCP's in surface waters.

4.2.2 Photolysis

Information on the photoreactivity of TCP's is sparse. Freitag et al. (1982) reported 66% photomineralization of 2,4,6-TCP after 17 hours under 290 nm ultraviolet light. In the presence of an electron acceptor, 2,4,6-TCP can be photooxidized to 2,6-dichlorophenoxyl semiquinone radical ion (Leaver 1971). The U.S. EPA (1979) concluded that the importance of photolysis in the degradation of TCP's in the environment is unknown.

4.2.3 Microbial Degradation

Several studies have examined biodegradation of TCP's in aquatic and soil systems. In a freshwater nutrient medium, Kreuk and Hanstveit (1981) observed 70% biodegradation of 2,4,5-TCP in 35 days and of 2,4,6-TCP in 9-18 days. Initial concentrations in this experiment were 1 mg/L. Using bacterial cultures, Tabak et al. (1964) measured 95% degradation of 2,4,6-TCP (initial concentration 300 p.p.m.) after 7 to 10 days. At an initial concentration of 100 p.p.m., 70% degradation was observed in 3 hours. In a study to determine the compatibility of wood preservatives and biological sewage treatment systems, Pauli and Franke (1972) reported no degradation of 2,4,5-TCP after 14 days exposure. Ingols et al. (1966) reported complete aromatic ring degradation of 2,4,6-TCP within five days by acclimated sludge. In a study to examine degradation of 2,4,6-TCP in soil, Alexander and Aleem (1961) reported complete disappearance of this compound from various soils in 1 to 9 days. Chu (1972) tested the growth of a Gram-variable bacillus on 19 chlorophenols and an unsubstituted phenol. Only 2,3,4,6-tetrachlorophenol and 3,4,6-TCP supported growth.

The U.S. EPA (1979) hypothesized that genetic induction levels for most degradative organisms would only be reached near discharges of TCP. Thus, stagnant waters with relatively high levels of TCP would support the appropriate microflora for rapid degradation. In fast-flowing waters, rapid dilution would tend to inhibit microbial adaptation. However, the more recent work of Kreuk and Hanstveit (1981) would suggest natural biodegradation under certain conditions of 70% in 9 to 35 days in natural waters.

4.2.4 Chemical Degradation

Specific information on the chemical degradation of TCP's in water or soil is lacking. Morrison and Boyd (1973) inferred that TCP's might undergo oxidation reactions when hydroxyl radicals attack C-2 and C-4 positions resulting in complex mixtures. NRCC (1982) suggested that the importance of oxidation of CP's in the environment should be re-examined. Hydrolysis of TCP's in the environment is probably insignificant due to the general resistance of a substituent attached to an aromatic ring to hydrolysis reactions (Morrison and Boyd 1973). The U.S. EPA (1979) concluded that chemical degradation is probably not important in controlling the fate of 2,4,6-TCP in surface waters.

4.2.5 Sorption Processes

The log octanol-water partition coefficients (log P) for TCP's are relatively high (3.72 for 2,4,5-TCP, 3.38 for 2,4,6-TCP; Table 4-1) and indicate a considerable potential for sorption by organic materials in sediments. In an aquarium ecosystem of biota and sediments receiving doses of 2,4,6-TCD to give a water concentration of 0.5 ug/L, Virtanen and Hattula (1982) observed a sediment-water distribution coefficient of 220-259 on a dry sediment organic content basis at 21-36 days following initial contaminant addition. Depuration from sediments followed gradual declines in contaminant levels in water. Wegman and Broek (1983) measured levels of all six TCP isomers in 17 sediment samples and 13 water samples from the Rhine River mouth area and reported the results shown in Table 4-2. These results provide evidence that TCP's with the possible exception of the 2,3,6-isomer, tend to accumulate in sedimentary sinks in aquatic systems. Sediment enrichment factors were 15 to 43 times relative to water levels. Data on sediment quality (particle size, organic content) and information on whether water samples were filtered prior to analysis were not provided. In a contaminated Finnish lake, Paasivirta et al. (1980) reported mean levels of 2,4,6-TCP in sediments of

10.4-17.2 ug/kg dry weight. Data on other sediment quality parameters and on water column concentrations were not given.

4.2.6 Volatilization

Compounds such as TCP's which are appreciably soluble and have relatively low vapour pressures (Table 3-1) do not generally volatilize from water (U.S. EPA 1979). The TCP's are moderately acidic and will be substantially ionized and solvated in natural surface waters. The U.S. EPA (1979) concluded that volatilization of 2,4,6-TCP is probably an insignificant process in environmental transport. This conclusion should hold true for other TCP isomers.

4.2.7 Bioaccumulation

Although the U.S. EPA (1979) found no data concerning bioaccumulation of TCP's, several studies were found in this review. A summary of data on bioaccumulation and depuration of TCP's in aquatic biota is provided in Table 4-3. Tabulated data show a range of bioconcentration factors spanning one order of magnitude for 2,4,5-TCP and two orders for 2,4,6-TCP. Variation is due to species and to study design. Tissue clearance rates are generally rapid, with estimated half-lives in fish ranging from 12h to less than 10 days.

Virtanen and Hattula (1982) observed bioaccumulation and depuration of 2,4,6-TCP in aquarium ecosystems. Test aquaria were spiked to 0.5 ug/L weekly over three weeks and concentrations were measured periodically during the contamination phase and following discontinuation of contaminant addition in water, sediment, invertebrates, plants and fish. Maximum bioconcentration factors (BCF's) were 1,720 for Oedogonium, 1,000 for Echinodorus, 4,460 for Elodea, 3,020 for Lymnaea (shell-free basis), 7,000 for male Poecilia reticulata, 12,180 for female P. reticulata and 1,020 for offspring P. reticulata. Uptake and depuration was rapid in Elodea and slower in Echinodorus and Oedogonium. Snails showed rapid uptake and achieved peak tissue levels in one week. Higher rates of uptake were observed in offspring than in adults. Depuration in snails was initially rapid but declined with time. Uptake in guppies was rapid with males showing a lower BCF and a faster rate of depuration than females. The data presented suggest a half-life in guppies of about 5 days.

Saarikoski and Viluksela (1982) exposed guppies to sublethal concentrations of 2,4,5-TCP at pH 6 and 26°C. A maximum tissue concentration was achieved within 24h and a BCF of 170 was determined.

Call et al. (1980) investigated the uptake and elimination of 2,4,5-TCP by young fathead minnows, Pimephales promelas. Experiments were undertaken in Lake Superior water (total alkalinity 40.0-43.2 mg/L as CaCO₃, pH 7.36-7.62, dissolved oxygen 8.02-8.42 mg/L, temperature=22°C). Fish were exposed for 28 days to mean concentrations of 4.8 ug/L and 49.3 ug/L. Concentrations of 2,4,5-TCP in water and fish were measured periodically. Uptake rates of 0.2 and 3.4 ug.g⁻¹.h⁻¹ were measured at the lower and higher concentrations, respectively. The maximum BCF's of 1,900 for the lower concentration and 1,800 for the higher concentration were attained within 1 to 2 days. Following the discontinuation of exposure conditions, depuration was rapid with a biological half life of 12h.

Freitag et al. (1982) exposed an alga (Chlorella fusca) and fish (Leuciscus idus melanotus) to 2,4,6-TCP for 24h and 3 days, respectively. Exposure conditions were 50 ug/L for the alga and 30 ug/L for the fish in 20-25°C water. Contaminant levels in the test water were measured during the experiments. BCF values were 51 for Chlorella and 310 for Leuciscus.

In Sweden, Landner et al. (1977) exposed yearling rainbow trout to diluted kraft pulp mill effluents after different treatment processes. Tissue concentrations of 2,4,6-TCP were found to be higher in liver than in muscle. Rates of uptake or depuration could not be calculated but a biological half-life of less than 10 days was estimated.

Other studies have reported tissue residues of TCP's in fish captured in contaminated environments. In contaminated Finnish lakes, Paasivirta et al. (1980) observed mean tissue levels of 2,4,6-TCP of 13.6-17.3 ug/kg in pike, 4.67-55.9 ug/kg in roach, 1.44 ug/kg in clams, 4.96-6.86 ug/kg in sponge and 0-2.45 ug/kg in plankton. Concentrations in water were not measured. Bacon (1978) reported 2,4,6-TCP levels in tissues of various marine invertebrates and fish near a pulp mill discharge at St. John, N.B. No chlorophenols were detected in water samples. The maximum tissue level reported was 3.8 ug/g of lipid in tomcod, with higher levels in fish generally found in liver, viscera and skin/fat than in muscle.

Based on log P-log BCF correlations given by Neely *et al.* (1974), Veith *et al.* (1979) and Mackay (1982), and on log P values of 3.72 for 2,4,5-TCP (Mackay 1982) and 3.38 for 2,4,6-TCP (Leo *et al.* 1971), theoretical BCF's for 2,4,5-TCP are 198-290 and for 2,4,6-TCP are 115-149.

Assuming a mean theoretical bioconcentration factor of 245 for 2,4,5-TCP and 130 for 2,4,6-TCP (Table 4-3) and using the uptake and clearance model of Neely (1979), uptake rate constants of 2.7 and 2.5 (k_1 values) and clearance rates of 0.011 h^{-1} and 0.019 h^{-1} for 2,4,5- and 2,4,6-TCP, respectively, are calculated. These rates of clearance are relatively rapid, and are equivalent to residence times of 89 h for 2,4,5-TCP and 53 h for 2,4,6-TCP. While calculated clearance rates are constant, depuration rates may decrease as tissue contaminant levels become low. This was reported in snails by Virtanen and Hattula (1982).

4.2.8 Probable Fate

Biodegradation of TCP's has been demonstrated and is probably important in the aquatic environment. Bioconcentration factors are high in plants, fish and invertebrates, but biological half-lives are relatively short. Sediment enrichment of most isomers has been reported and sedimentation of suspended particulates is probably a significant process of removal of TCP's from the water column. Photolysis, chemical degradation and volatilization are thought to be insignificant processes in natural surface waters. The overall environmental half-life is estimated at 9-18 days for 2,4,6-TCP and 35 days for 2,4,5-TCP in stagnant surface waters. TCP's may be more persistent under high dilution or high flow conditions. Because TCP's appear to have environmental half-lives of less than eight weeks, these compounds are treated as non-persistent in the development of water quality criteria (Section 4.4.5). Table 4-4 summarizes the aquatic fate of TCP's.

4.3 Distribution in Ontario

Little information exists on environmental concentrations of TCP in Ontario surface waters. Of 10 water samples from Thunder Bay near a pulp mill discharge, two had levels of 3 and 23 $\mu\text{g/L}$ TCP (Robinson and Smillie 1977). No TCP's were detected in 11 water samples from the St. Mary's River near a pulp and paper discharge at Sault St. Marie. The Ontario Ministry of the Environment reported concentrations of 2,4,6-TCP in

Jackfish Bay, Lake Superior at varying distances from a pulp and paper wastewater discharge (C. Cherwinsky, Water Resources Branch, pers. comm.). Concentrations progressively decreased with increasing distance from the source and ranged from 3.3 ug/L, 30 m from the discharge, to 0.20 ug/L, 1.53 km from the discharge. Because of the potential diversity of sources of TCP's, particularly the 2,4,5- and 2,4,6-isomers, the occurrence of these compounds in Ontario may be widespread.

4.4 Effects on Aquatic Organisms

Biological effects information is available for four of the six trichlorophenol (TCP) isomers. Most of the data, however, pertains to 2,4,5-TCP and 2,4,6-TCP. The former is used extensively in chemical manufacturing as a feedstock for production of various pesticides and herbicides. 2,4,6-TCP is usually present in the environment as a breakdown metabolite of other chlorinated compounds (U.S. EPA, 1980a). The highly toxic 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) is often found as a contaminant by-product of 2,4,5-TCP and the final pesticides products produced.

The majority of toxicity data available on the TCP group were obtained from static bioassays in which contaminant concentrations were calculated rather than measured. Relevant data on acute and chronic effects are given in Tables 4-5 to 4-10. This information is summarized and compared to various regulatory standards in Figure 4-1.

4.4.1 Acute Toxicity

An abundance of good quality acute toxicity information exists on the effects of 2,4,5- and 2,4,6-TCP on fish and invertebrates (Tables 4-5 and 4-6). Ninety-six hour LC₅₀ values for 2,4,5-TCP range from 3,060 ug/L for guppy (Saarikoski and Viluksola 1981) to 450 ug/L for bluegill (Buccafusco et al. 1981), and it would appear from this data that sensitive invertebrates respond at levels similar to fish (LeBlanc 1980). The toxicity of 2,4,6-TCP is in the same order of magnitude, with bluegills and rainbow trout showing greater sensitivity than fatheads or Daphnia magna. LC₅₀ values ranged from 320 ug/L (Buccafusco et al. 1981) to 9,700 ug/L (Phipps et al. 1981) in 96-hour tests.

As with other chlorophenol isomers, studies have been conducted to establish the influence of pH on 2,4,5- and 2,4,6-TCP toxicity. Saarikoski and Viluksela (1981) using

guppies found a decrease in toxicity with increasing pH. This pattern was also observed by PPRIC (1979) on experiments with rainbow trout.

4.4.2 Chronic Toxicity

At the time of this review, chronic information on only 2,4,6-TCP was available. The U.S. EPA reported an early life stage bioassay using fathead minnows in which the chronic threshold for effect was 720 ug/L. Clearly, this value does not protect against acute effects in more sensitive species based on acute data for other TCP isomers. A second toxicity study of questionable value to this report¹ was conducted by Virtanen and Hattula (1982) who described a 10-month partial life cycle study using guppies.

4.4.3 Plant Toxicity

A limited number of studies were available for review on the toxicity of TCP isomers to aquatic plants. Huang and Gloyna (1968) showed that 2,4,6-TCP caused destruction of chlorophyll in the green alga Chlorella pyrenoidosa at 10 mg/L. Blackman et al. (1955) found chlorosis in duckweed (Lemna minor) after 72 hour exposure to 5,920 ug/L of 2,4,6-TCP.

4.4.4 Flavour Impairment

Tainting studies have been conducted only for 2,4,6-TCP. Threshold concentrations were observed at 52 ug/L (Shumway and Palensky 1973), an order of magnitude less than the most sensitive acute toxicity response. This suggests that the gap in concentration between acutely toxic and tainting effects is less for TCP than those observed for MCP and DCP isomers. Thus, tainting does not appear to be as critical for TCP as it is for MCP and DCP.

¹Information on experimental design was lacking.

4.4.5 Criteria Development

The U.S. EPA (1980a) derived criteria for the protection of aquatic life by means of two approaches. The first was a maximum 'not-to-exceed' level based on acute toxicity data, and the second was a 24-hour average level based on chronic effect data. Insufficient information was available on TCP effects to develop U.S. EPA criteria. Since that time, tainting and chronic toxicity data have become available for 2,4,6-TCP and good acute toxicity data are available for the 2,4,5-TCP isomer. For 2,4,5- and 2,4,6-TCP, the most sensitive species tested in terms of acute effects was the bluegill. Considering both isomers, the geometric mean acute toxicity value for bluegills was 379 ug/L.

TCP is considered non-persistent in the environment (Section 4.2.8); therefore, a safe level based on toxic effects is estimated based on the geometric mean LC₅₀ of the most sensitive species (379 ug/L) multiplied by the application factor of 0.05 for non-persistent contaminants. The product, 18.95 ug/L, is less than half of the lowest tainting threshold (Table 4-10), and thus in keeping with the approach outlined in Section 1.4, a criterion of 18 ug/L is recommended to protect against both chronic toxicity and tainting of fish flesh from TCP in the environment.

TABLE 4-1: PHYSICAL PROPERTIES OF TRICHLOROPHENOLS
(adapted from Jones 1981)

CAS No.	Compound	Commercial utility	Formula	Molecular Weight	Boiling point ^a (760 mm or as stated), °C	Melting point ^a (°C)	Dissociation constant ^b at 25°C, K _a
15950660	2,3,4-TCP	No	C ₆ H ₃ Cl ₃ O	197.45	sublimes	83.5	2.2x10 ⁻⁸
933788	2,3,5-TCP	No	"	"	248.5-249.5(250)	62	4.3x10 ⁻⁸
933755	2,3,6-TCP	No	"	"	272 ^b ; 246 ^h	58	7.4x10 ⁻⁸
95954	2,4,5-TCP	Yes	"	"	sublimes(275 ^b)	68-70.5	3.7x10 ⁻⁸
88062	2,4,6-TCP	Yes	"	"	246	69.5	3.8x10 ⁻⁸
609198	3,4,5-TCP	No	"	"	271-7(746)	101	1.8x10 ⁻⁸

Compound	pK ^{c,e}	pK ^d	Water solubility ^e (pH 5.1, 25°C) (moles/L)	Density ^{a,f}	Vapour Pressure ^g @°C	Log P	Flash Pt. ^g °C	Appearance
2,3,6-TCP	-	5.98	-	-	-	-	-	-
2,4,5-TCP	7.0	7.07	4.8x10 ⁻³	-	1mm@72C	3.72 ⁱ	-	Colorless needles, or grey flakes
2,4,6-TCP	6.1	6.62	2.2x10 ⁻³ (800 mg/L@25°C) ^h	1.490 ⁷⁵ /4	1mm@53.0C; @76.5C ^h	3.38 ^j	113.9	Colorless crystals
3,4,5-TCP	-	7.83	-	-	-	-	-	-

^a Weast (1974)

^b Doedens (1967)

^c Pearce and Simpkins (1968)

^d Farquharson et al (1958)

^e Blackman et al (1955)

^f Density is relative to water, the superscript indicates the temperature of the liquid and the subscript the temperature of the water to which the density is referred.

^g Sax (1975)

^h Kingsbury et al. (1979)

ⁱ Mackay (1982)

^j Leo et al. (1971)

TABLE 4-2: CONCENTRATIONS (ppb) OF TRICHLOROPHENOLS IN SEDIMENT
AND WATER FROM THE LOWER RHINE RIVER
(from Wegman and Broek 1983)

	Sediment			Water		
	Frequency (%)	Max.	Median	Frequency (%)	Max.	Median
2,3,4-TCP	18	0.8	0.7	8	0.04	-
2,3,5-TCP	100	11	2.4	38	0.28	-
2,3,6-TCP	0	-	-	46	0.36	-
2,4,5-TCP	100	15	6.4	77	0.32	0.15
2,4,6-TCP	94	3.7	1.9	100	0.74	0.13
3,4,5-TCP	82	19	1.2	54	0.31	0.05

TABLE 4-3: BIOCONCENTRATION FACTORS AND DEPURATION RATES FOR
2,4,5-TRICHLOROPHENOL AND 2,4,6-TRICHLOROPHENOL IN
FRESHWATER BIOTA

	BCF	Depuration	Reference
<u>2,4,5-TCP</u>			
<u>Poecilia reticulata</u>	170	-	1
<u>Pimephales promelas</u>	1,800-1,900	$T_{1/2}=12\text{h}$	2
Fish (calculated)	198	Clearance rate= 0.011 h^{-1}	3,4
	290		5
	252		6
<u>2,4,6-TCP</u>			
<u>Elodea</u>	4,460	rapid	7
<u>Oedogonium</u>	1,720	slower	7
<u>Echinodorus</u>	1,000	slower	7
<u>Chlorella fusca</u>	51	-	8
<u>Lymnaea</u>	3,020	initially rapid, then declining	7
<u>Poecilia reticulata</u>			
- male	7,000	$T_{1/2}\sim 5\text{ days}$	7
- female	12,180	(our estimate)	
- juvenile	1,020		
<u>Leuciscus idus melanotus</u>	310	-	8
<u>Salmo gairdneri</u>	-	$T_{1/2}= <10\text{ days}$	9
Fish (calculated)	115	Clearance rate= 0.019 h^{-1}	3,4
	149		5
	125		6

¹ Saarikoski and Viluksela (1982)
² Call et al. (1980)
³ Neely et al. (1974)
⁴ Neely (1979) (see text for assumptions)

⁵ Veith et al. (1979)
⁶ Mackay (1982)
⁷ Virtanen and Hattula (1982)
⁸ Freitag et al. (1982)
⁹ Landner et al. (1977)

TABLE 4-4: SUMMARY OF AQUATIC FATE OF TRICHLOROPHENOLS
(adapted from U.S EPA 1979)

Environmental Process	Summary Statement	Rate	Half Life	U.S. EPA's Confidence of Data
<u>Degradation Processes</u>				
Photolysis	- process has been reported; environmental relevance unknown.	-	-	low
*Biodegradation	- reported in water, soil and bacterial cultures; probably occurs more readily in stagnant waters than in dilute or flowing systems.	-	70% degradation of 2,4,5-TCP: 35 days; 70% degradation of 2,4,6-TCP: 9-18 days in stagnant water	medium
Chemical Degradation	- oxidation and hydrolysis reactions are probably insignificant.	-	-	low
<u>Transport Processes</u>				
*Sorption	- probably important based on log P of 3.72 for 2,4,5- and 3.38 for 2,4,6-TCP; sediment enrichment observed in Rhine River and Finnish lake sediments.	-	sediment accumulation and depuration relatively rapid (days) in laboratory tests	medium
Volatilization	- not considered important in natural surface waters.	-	-	low
Bioaccumulation	- 2,4,5-TCP: BCF = 170-1,900 (fish); - 2,4,6-TCP: BCF = 51-4,420 (plants), 115-12,180 (fish), 3,000 (invertebrates).	- uptake rates rapid to moderate (hours to days).	- $T_{1/2}$ = 12 h- <10 days	high

Probable overall environmental half-life

≥9 to ≥35 days

*Probable dominant processes in degradation and removal.

TABLE 4-5: PRIMARY ACUTE TOXICITY DATA FOR THE TRICHLOROPHENOLS

Isomer Evaluated	Species	Method ¹	Individual Results (ug/L)	Geometric Mean (ug/L)	Test Laboratory Water Quality			Laboratory	Reference
					Mean pH	Mean Temp. (°C)	Hardness (as CaCO ₃ mg/L)		
2,4,5-TCP	Cladoceran <u>Daphnia magna</u>	48 hr-LC ₅₀ , S,U	2,660	2,660	8.0	22	173	EG & G Bionomics, Mass.	LeBlanc 1980
	Guppy <u>Poecilia reticulata</u>	96 hr-LC ₅₀ , Semi S,M	990 1,240 3,060	1,700	6.0 7.0 8.0	26 26 26	90 90 90	Dept. of Zool. Univ. of Helsinki Finland	Saarikoski and Yiluksela 1981 ⁴
	Bluegill <u>Lepomis macrochirus</u>	96 hr-LC ₅₀ , S,U	450	450	7.2	22	40	EG & G Bionomics, Mass.	Buccafusca et al. 1981 ^{2,3}
2,4,6 TCP	Cladoceran <u>Daphnia magna</u>	48 hr-LC ₅₀ , S,U	6,040	6,040	8.0	22	173	E, G & G Bionomics, Mass.	LeBlanc 1980
	Rainbow Trout <u>Salmo gairdneri</u>	96 hr-LC ₅₀ , S,U	450		6.4	12	280	Pulp & Paper Res. Inst. Pt. Claire, Que.	PPRIC 1979
		96 hr-LC ₅₀ , S,U	2,600	1020	7.7	12	280		"
	Fathead Minnow <u>Pimephales promelas</u>	96 hr-TLm, S,U	100-1000					-	Barnhart & Campbell 1972
		96 hr-LC ₅₀ , S,M	600					-	U.S. EPA 1972
		96 hr-LC ₅₀ , FT,M	9,700 8,600	2240	7.5 7.5	23 23	45 45	U.S. EPA Env. Res. Lab., Duluth, Minn.	Phipps et al. 1981 ³

TABLE 4-5: PRIMARY ACUTE TOXICITY DATA FOR THE TRICHLOROPHENOLS (Cont'd)

Isomer Evaluated	Species	Method ¹	Test Laboratory Water Quality					Laboratory	Reference
			Individual Results (ug/L)	Geometric Mean (ug/L)	Mean pH	Mean Temp. (°C)	Hardness (as CaCO ₃ mg/L) ³		
2,4,6-TCP	<u>Guppy</u> <u>Poecilia</u> <u>reticulata</u>	96 hr-LC ₅₀ , Semi S,M	610	2,850	5.0	26	90	Dept. of Zool., Univ. of Helsinki Finland "	Saarikoski & Viluksela 1981 ⁴ " "
			890		6.0	26	90		
			2,290		7.0	26	90		
			7,860		8.0	26	90		
	<u>Bluegill</u> <u>Lepomis</u> <u>macrochirus</u>	96 hr-LC ₅₀ , S,U	320	320	7.2	22	40	E,G & G Bionomics, Mass.	Buccafusco et al. 1981 ^{2,3}

¹Terms: FT = flow-through bioassay, Semi S.= Static bioassay with solution replacement, S = static bioassay,
U = test tank concentrations unmeasured, M = test tank concentrations measured, SW = water of low hardness
MW = water of medium hardness, HW = water of high hardness

²Conductivity reported

³Alkalinity reported

⁴Major ions reported

TABLE 4-6: SECONDARY ACUTE TOXICITY DATA FOR THE TRICHLOROPHENOLS

Isomer Evaluated	Species	Method	Results (ug/L)	Test Laboratory Water Quality			Laboratory	Reference
				Mean pH	Mean Temp. (°C)	Mean Hardness (as CaCO ₃ mg/L)		
2,3,5-TCP	Brown Trout <u>Salmo trutta</u>	24 hr-LC ₅₀ ,S,U	800	-	5	-	Dept. of Cell Biology, Univ. of Jyvaskyla, Finland	Hattula <u>et al.</u> 1981
2,4,5-TCP	Rainbow Trout <u>Salmo gairdneri</u>	48 hr-LC ₅₀ ,FT,U	1,000	15	SW	259	Oak Creek Fish. Lab, Oregon State Univ., Corvallis	Shumway & Palensky 1973
		24 hr-LC ₁₀₀ ,S,U	5,000	-	12.8	-	U.S. Fish & Wild. Serv., Ann Arbor Michigan	Applegate <u>et al.</u> 1957
	Brown Trout <u>Salmo trutta</u>	12 hr-LC ₅₀ ,S,U	900	-	5	-	Dept. of Cell Biology, Univ. of Jyvaskyla, Finland	Hattula <u>et al.</u> 1981
	Goldfish <u>Carassius auratus</u>	24 hr-LC ₅₀ ,S,U	1,700	-	-	-	-	Kobayshi <u>et al.</u> 1979
	Bluegill <u>Lepomis macrochirus</u>	2 hr-LC ₁₀₀ ,S,U	5,000	-	17	-	U.S. Fish & Wild. Serv., Ann Arbor Michigan	Applegate <u>et al.</u> 1957
	Lymnaeid Snails	24 hr-LC ₁₀₀ ,S,U	10,000	-	-	-	Florida Agric. Exp. Stn., Fla.	Batte & Swanson 1952

TABLE 4-6: SECONDARY ACUTE TOXICITY DATA FOR THE TRICHLOROPHENOLS (Cont'd)

Isomer Evaluated	Species	Method	Results (ug/L)	Test Laboratory Water Quality			Laboratory	Reference
				Mean pH	Mean Temp. (°C)	Mean Hardness (as CaCO ₃ mg/L)		
2,4,5-TCP	Sea Lamprey (larvae) <u>Petromyzon marinus</u>	2 hr-LC ₁₀₀ ,S,U	5,000	-	12.8	-	U.S. Fish & Wild. Serv., Ann Arbor, Michigan	Applegate <u>et al.</u> 1957
	Northern Squawfish <u>Ptychocheilus oregonensis</u>	1 hr-LC ₁₀₀ ,S,U	10,000	-	10.6	-	Forest, Wild. & Range Exp. Stn., Univ. of Idaho	MacPhee & Ruelle 1969
	Chinook Salmon <u>Oncorhynchus tshawytscha</u>	1 hr-LC ₁₀₀ ,S,U	10,000	-	10.6	-	"	"
	Coho Salmon <u>Oncorhynchus kisutch</u>	1 hr-LC ₁₀₀ ,S,U	10,000	-	10.6	-	"	"
2,4,6-TCP	Lymnaeid Snails	24 hr-LC ₁₀₀ ,S,U	5,000	-	-	-	Florida Agr. Exp. Stn., Florida	Batte & Swanson 1952
	Brown Trout <u>Salmo trutta</u>	24 hr-LC ₅₀ ,S,U	1,100	-	5	-	Dept. of Cell Biology, Univ. of Jyvoskyla, Finland	Hattula <u>et al.</u> 1981
	Goldfish <u>Carassius auratus</u>	24 hr-LC ₅₀ ,S,U	10,000	-	-	-	-	Kobayashi <u>et al.</u> 1979

¹Terms: FT = flow-through bioassay, S = static bioassay, U = test tank concentrations unmeasured
SW = water of low hardness

TABLE 4-7: PRIMARY CHRONIC TOXICITY DATA FOR THE TRICHLOROPHENOLS

Isomer Evaluated	Species	Method ¹	Test Conc. Ranges (ug/L)	Conc. of Lowest Chronic Effect (ug/L)	<u>Test Laboratory Water Quality</u>				Laboratory	Reference
					Mean pH	Mean Temp. (°C)	Hardness (as CaCO ₃ mg/L)			
2,4,6-TCP	Fathead Minnow <u>Pimephales</u> <u>promelas</u>	Early Life Stage FT, M	530-970	720	-	-	-	-		U.S. EPA 1978

¹Terms: FT = flow-through bioassay, Semi S.= Static bioassay with solution replacement, S = static bioassay,
 U = test tank concentrations unmeasured, M = test tank concentrations measured, SW = water of low hardness
 MW = water of medium hardness, HW = water of high hardness

TABLE 4-8: SECONDARY CHRONIC TOXICITY DATA FOR THE TRICHLOROPHENOLS

Isomer Evaluated	Species	Method ¹	Results (ug/L)	Test Laboratory Water Quality			Laboratory	Reference
				Mean pH	Mean Temp. (°C)	Hardness (as CaCO ₃ mg/L)		
2,3,6-TCP	Crayfish <u>Astacus fluviatilis</u>	8 day-LC ₅₀ , S,U	5,400	6.5	13	-	-	Kaila & Saarikoski 1977
			19,000	7.5	13	-	-	
• 2,4,6-TCP	Fathead Minnow <u>Pimephales promelas</u>	8 day-LC ₅₀ , FT, M	5,800	7.5	23	45	U.S. EPA Env. Res. Lab. Puluth, Minn.	Phipps <u>et al.</u> ³ 1981
			6,400	7.5	23	45		

¹Terms: FT = flow-through bioassay, Semi S.= Static bioassay with solution replacement, S = static bioassay, U = test tank concentrations unmeasured, M = test tank concentrations measured, SW = water of low hardness, MW = water of medium hardness, HW = water of high hardness

²Conductivity reported

³Alkalinity reported

TABLE 4-9: PLANT VALUES FOR TRICHLOROPHENOLS

Isomer Evaluated	Species	Method	Results (ug/L)	Test Laboratory Water Quality			Laboratory	Reference
				Mean pH	Mean Temp. (°C)	Mean Hardness (as CaCO ₃ mg/L)		
2,4,5-TCP	Alga <u>Selenastrum capricornutum</u>	96 hr-EC ₅₀ chlorophyll a	1,220	-	-	-	-	U.S. EPA 1978
	Duckweed <u>Lemna minor</u>	Chlorosis 72hr-LC ₅₀	5,923	5.1	25	-	Dept. of Agric., Oxford Univ., England	Blackman <u>et al.</u> 1955
2,4,6-TCP	Duckweed <u>Lemna minor</u>	Chlorosis	5,923	5.1	25	-	"	"
2,4,5- & 2,4,6-TCP	Alga <u>Chlorella pyrenoidosa</u>	Complete destruction of	10,000	-	-	-	Civil Eng. Dept., Univ. of Texas	Huang & Gloyna 1978

TABLE 4-10: FISH TAINTING VALUES FOR THE TRICHLOROPHENOLS

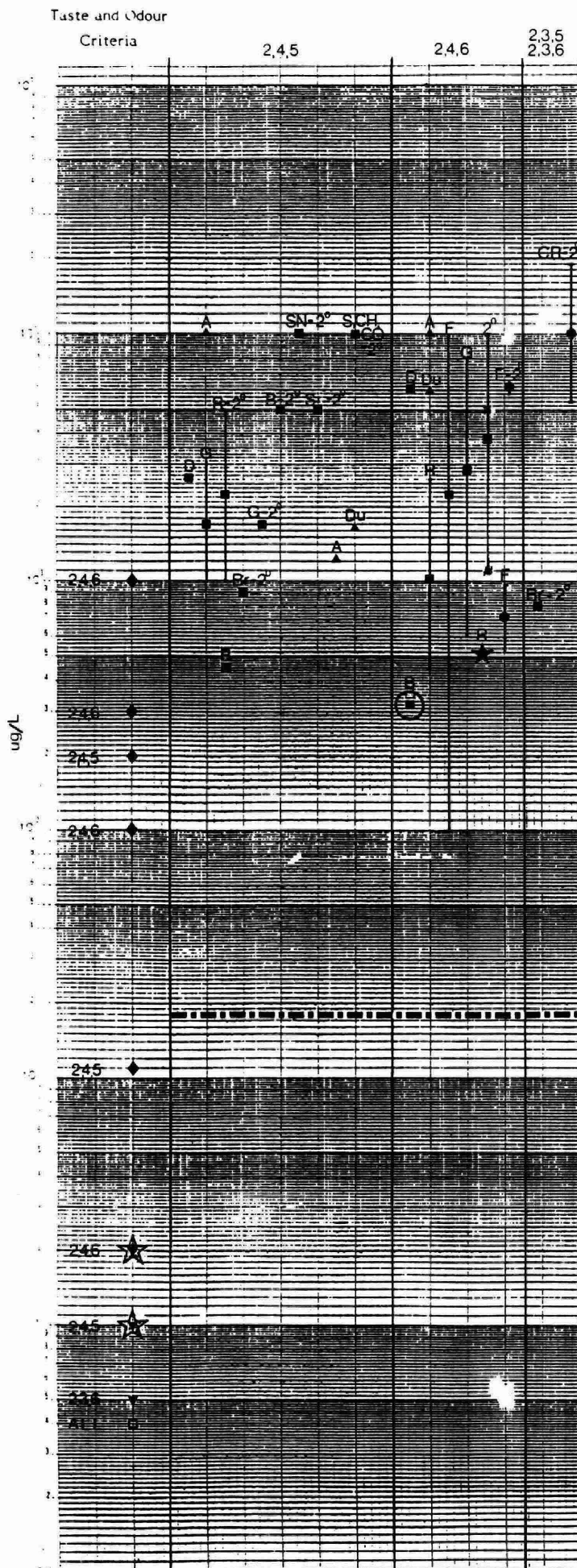
Isomer Evaluated	Species	Method ¹	Est. Flavour Impairment Threshold (ug/L)	Test Laboratory Water Quality			Laboratory	Reference
				Mean pH	Mean Temp. (°C)	Mean Hardness (as CaCO ₃ mg/L)		
2,4,6-TCP	Rainbow Trout <u>Salmo gairdneri</u>	ETC,FT,U	52	7.5	15	SW	Oak Cr. Fisher. Lab., Oregon St. Univ., Corvallis	Shumway & Palensky, 1973 ^{2,4}

¹Terms: FT = flow-through bioassay, U = test tank concentrations unmeasured, SW = low water hardness, ETC = estimated threshold concentrations

²Conductivity reported

³Alkalinity reported

⁴Major ions reported



CODES

- ◆ Odour Threshold
- ▼ Taste Threshold
- Acute Toxicity
- Chronic Toxicity
- ▲ Plant Data
- ★ Tainting (Fish Flesh)
- ☆ EPA Criteria
- Soviet Criteria
- 2° Secondary Data
- Recommended Criterion
- Vertical bars represent data ranges
- Critical Value in Criteria Selection

Test Species

- Du Duckweed
- A Alga
- D Daphnia
- B Bluegill
- G Goldfish
- R Rainbow Trout
- Br Brown Trout
- Gu Guppy
- CH Chinook Salmon
- CO Coho Salmon
- S Sea Lamprey
- CR Crayfish
- SN Snails
- F Fathead Minnow

Routine detection limits
MOE, December 1983:
2,3,4 - TCP: 100 ng/L.
other TCP's: 50 ng/L

FIGURE 4-1:
TRICHLOROPHENOLS
TOXICITY AND CRITERIA SUMMARY

Recommended Criterion 18 ug/L

5.0 TETRACHLOROPHENOLS

There are three important isomers of tetrachlorophenol (TTCP):

2,4,3,5-tetrachlorophenol	(2,3,4,5-TTCP)
2,3,4,6-tetrachlorophenol	(2,3,4,6-TTCP)
2,3,5,6-tetrachlorophenol	(2,3,5,6-TTCP)

5.1 Occurrence

Of the three isomers of tetrachlorophenol, only 2,3,4,6-TTCP has commercial utility (Jones 1981). Two other possible isomers (2,4,5,6- and 3,4,5,6-TTCP) are rarely mentioned in the literature and are probably of negligible importance. Most available information on environmental behaviour and aquatic toxicology concerns the 2,3,4,6-isomer. 2,3,4,6-TTCP was manufactured (until July 1983) in Canada by:

Uniroyal Limited
Clover Bar, Alberta

and is distributed by:

Bayer (Canada) Ltd.
through Dow Chemical of Canada Ltd.
P.O. Box 1012, Highway #40
Sarnia, Ontario. N7T 7K1

The 2,3,4,6-isomer of TTCP is usually used along with pentachlorophenol (PCP) as an active ingredient in wood preservatives. Commercial PCP usually contains 3 to 10% TTCP. The lower CP's including TTCP are generally less desirable than PCP in wood treatment because of their undesirable odours, higher volatilities and solubilities and their dermal irritant properties.

Biocides containing 2,3,4,6-TTCD may contain the toxic impurities polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) (Jones 1981). The environmental behaviour and toxicology of these impurities will not be discussed in this report.

TTCP occurs primarily in wastes from wood preserving industries. Garrett (1980) reported TTCP in discharges from forest products industries and concentrations were highest (up to 2,100 ug/L) in a laminated wood manufacturer discharge. Fox and Joshi (1984) reported 2,3,4,6- and 2,3,5,6-TTCP, in combination with PCP, in the Trent River and Bay of Quinte (Ontario), downstream from a wood-treatment facility. Very little direct effluent was produced by the plant and contamination was attributed to weathering of excess wood preservative in the lumber yard. Environment Canada (1979a) observed 2,3,4,6-TTCP in laboratory-prepared bleach effluents from softwood and hardwood pulping processes.

Agricultural lands may provide diffuse sources of TTCP to surface waters. Commercial PCP/TTCP preparations are used in agriculture to prevent wood decay in farm buildings, fences, etc. In combination with some herbicides, commercial PCP/TTCP may also be used in weed control (Jones 1981).

While there are reports of lower CP formation during chlorination of water and sewage (eg. Campbell 1972), there are apparently no reports of TTCP formation by this means. Nonetheless, TTCP probably occurs widely in municipal sewage through introduction by industry. Garrett (1980) identified TTCP in Vancouver area sewage influent and effluent. Fox (1978) reported PCP in seven sewage treatment plant effluents in Ontario. The presence of PCP indicates the probable occurrence of TTCP in treated sewage.

Wastes from other industries and from landfill sites may also include TTCP's. Garrett (1980) measured a wide occurrence of TTCP in various landfill leachates and waste discharges in Greater Vancouver. No TTCP was reported in surface waters draining hazardous chemical landfills in Niagara Falls, New York (Elder et al. 1981).

Incineration of municipal refuse may provide a minor source of TTCP to the environment. Olie et al. (1977) detected unquantified levels of TTCP in flue gas from municipal incinerators. Fallout of TTCP from the atmosphere may result in entry to aquatic environments.

TTCP's may form in the environment as degradation products of PCP. Crosby and Hamadmad (1971) irradiated PCP in organic solvents with ultraviolet light, and reported

the formation of 2,3,5,6-TTCP plus a small amount of another phenolic substance assumed to be a TTCP isomer. Pierce and Victor (1978) observed the formation of 2,3,5,6- and 2,3,4,5-TTCP in a freshwater lake following a PCP spill and attributed their occurrence to degradation of PCP. TTCP is only one of several degradation products of PCP identified in the literature (see Jones 1981).

5.2 Environmental Fate

5.2.1 Physical and Chemical Properties

A summary of physicochemical properties of TTCP's is presented in Table 5-1. These properties control the behaviour of TTCP in surface water systems.

5.2.2 Photolysis

No studies describing photolysis of TTCP were discussed in reviews on CP's in the environment by Jones (1981), Buikema *et al.* (1979), Ahlorg and Thunberg (1980), the National Research Council of Canada (NRCC 1982), or U.S. EPA (1980a). No further information on photolysis of TTCP was found in this review. Photolysis has been demonstrated in MCP, DCP, TCP and PCP. In the three lower CP's, the environmental importance of photolysis is either low or unknown (Sections 2-3). Photodegradation of PCP to TTCP in surface waters is probably significant (Section 6). On the basis of our somewhat limited knowledge on these other CP's, it is reasonable to assume that TTCP's are susceptible to photodegradation to some uncertain extent in the natural environment.

5.2.3 Microbial Degradation

Fox and Joshi (1984) measured concentrations of 2,3,4,6- and 2,3,5,6-TTCP in various ecosystem components at the mouth of the Trent River and throughout the Bay of Quinte (Ontario) downstream of a wood preserving plant. In a sediment core collected from a relatively deep area of the bay, concentrations of TTCP and PCP decreased gradually with depth. This suggested either slow degradation or increasing loadings of wood preservatives over time. The authors noted that a remarkably constant TTCP:PCP ratio with depth in the core suggested increased loading and not degradation was responsible for the concentration change. A depositional period of 30 years was sampled in the core,

suggesting that these compounds are highly resistant to biodegradation in some sediments. Potentially anaerobic conditions in these organic rich sediments may have retarded the biodegradation process. If biodegradation was responsible for the decline in concentration with time, the half-life for removal by this process would appear to be in the order of five to ten years.

Pierce and Victor (1978) analyzed concentrations of 2,3,4,5-TTCP and 2,3,4,6-TTCP in water and sediment following a PCP spill into a small Mississippi lake. TTCP isomers appeared primarily as PCP breakdown products. Levels of 2,3,4,5-TTCP could not be accurately measured, but were "equal to or greater than" 2,3,5,6-TTCP concentrations. Both TTCP's were persistent in water and sediment and showed no discernible change in concentrations between January 5 just after the spill, and April 27, 1977 (about 3.5 months). High sediment concentrations (up to 235 ug/kg) of 2,3,5,6-TTCP were also measured in August and October 1976, 18 to 20 months after a prior spill. Unfortunately, environmental concentrations of TTCP were not followed immediately after the earlier spill. Results of this study are somewhat difficult to interpret. Nonetheless, microbial degradation appeared to be slow and the half-life for biodegradation was probably longer than 3.5 months in this case.

In soil, 2,3,4,5-TTCP degrades to 2,3,5-TCP, 2,4,5-TCP, 3,4-DCP and 3-CP; 2,3,4,6-TTCP to 2,4,5-TCP; and 2,3,5,6-TTCP to 2,3,5-TCP and 2,5,6-TCP (Cserjesi and Johnson 1972; Kuwatsuka 1972). Of 19 CP's providing sole carbon sources, only 2,3,4,6-TTCP and 2,4,6-TCP individually supported growth of a Gram-variable bacillus in culture (Chu 1972). Curtis *et al.* (1972) and Gee and Peel (1974) reported the formation of the tainting substance 2,3,4,6-tetrachloroanisole from 2,3,4,6-TTCP by fungi found in poultry litter.

5.2.4 Chemical Degradation

Data on abiotic chemical breakdown of TTCP's in soil and in water were unavailable in the literature reviewed in Jones (1981), NRCC (1982) and in this study. TTCP's might undergo oxidation reactions where hydroxyl radicals attack C-2 and C-4 positions resulting in complex chemical mixtures (Morrison and Boyd 1973). NRCC (1982) suggested that the process of oxidation in CP's should be studied further. Hydrolysis of TTCP's in the environment is likely insignificant because of the resistance of substituents attached to an aromatic ring to hydrolysis reactions (Morrison and Boyd 1973). The U.S.

EPA (1979) concluded that chemical degradation of MCP, DCP, TCP and PCP is probably unimportant in the aquatic environment. The same conclusion is valid for TTCP.

5.2.5 Sorption Processes

The log octanol-water distribution coefficients of TTCP's are high (log P , 2,3,4,6-TTCP=4.10; Table 5-1), indicating a high potential for accumulation in organic matter in water-column particulates and sediments. This potential is confirmed by data from contaminated systems, showing that TTCP accumulates in sediment.

Table 5-2a shows concentrations of TTCP (2,3,4,6 plus 2,3,5,6) in surface film, unfiltered water and sediment from the Bay of Quinte, downstream of a wood preserving facility (Fox and Joshi 1984). Sediments were enriched with TTCP by factors of 10-125 and 500-6,500 with respect to concentrations found in the surface film and water column, respectively.

Table 5-2b shows sediment and filtered water concentrations of 2,3,5,6-TTCP in a small Mississippi lake (Pierce and Victor 1978). PCP spills occurred in December 1974 and December 1976. The data show very high TTCP concentrations in sediment relative to water before the 1976 spill (sediment-water distribution coefficient: 280-2,800). Following this spill, dissolved TTCP levels increased by about an order of magnitude while no change in sediment TTCP levels was apparent.

Table 5-2c shows water and sediment concentrations of three TTCP isomers in the lower Rhine River (Wegman and Brock 1983). Water samples were apparently unfiltered. A sedimentary sink is indicated here for each of the three isomers.

In contaminated Finnish lakes, Paasivirta et al. (1980) reported mean 2,3,4,6-TTCP concentrations in sediments of 33.4-50.1 ug/kg dry weight. Although information on concentrations in water was not provided, these sediment concentrations are generally within the range of TTCP concentrations reported in contaminated sediments by Fox and Joshi (1984) and Pierce and Victor (1978).

5.2.6 Volatilization

TTCP's are appreciably soluble in water and have low vapour pressures (Table 4-1). Such compounds do not generally volatilize from water to a significant extent (U.S. EPA 1979). Also, TTCP's are weak acids and should be substantially dissociated and solvated in natural surface waters. Thus, it can be concluded that volatilization is not an important process for removal of TTCP's from water.

5.2.7 Bioaccumulation

Few studies have examined bioaccumulation of TTCP's in freshwater biota. Pierce and Victor (1978) provided the most important source of information on uptake of TTCP in fish. Table 5-3 summarizes available biological uptake and depuration data for TTCP.

Pierce and Victor (1978) measured concentrations of PCP, TTCP and breakdown products (anisoles) in a small lake in Mississippi following two accidental spills. Concentrations of 2,3,5,6-TTCP were measured in muscle and liver of sunfish, bass and catfish. Concentrations of TTCP in filtered water samples were also measured. TTCP concentrations in water before a December 1976 spill are provided in Table 5-2b. Mean concentrations for October 1976, January 1977 and April 1977 were 0.05, 0.99 and 1.17 ug/L, respectively. Mean concentrations and ranges (ng/g fresh weight) in fish tissues during the same months were:

	<u>Sunfish</u>		<u>Bass</u>		<u>Catfish</u>	
	Muscle	Liver	Muscle	Liver	Muscle	Liver
October 1976	1	40 (30-50)	-	-	-	-
January 1977	78 (60-95)	950	215 (130-250)	4,900 (1,600-8,200)	219	8,500
April 1977	25 (22-27)	200 (150-250)	-	-	62 (41-82)	1,170 (990-1,400)

From these mean fish tissue and water concentrations, bioconcentration factors (BCF's) of <20-221 for muscle tissue and 40-8,590 for liver tissue are calculated, as detailed in

Table 5-3. Highest values were reported in catfish. Based on a few samples, the authors noted that 2,3,5,6-TTCP was also present in all ecosystem components sampled, although absolute concentrations could not be defined.

Fox and Joshi (1984) measured TTCP concentrations (2,3,4,6 and 2,3,5,6) in leeches, chironomids and Cladophora from the Bay of Quinte. Concentrations in leeches and Cladophora were 40 and 5 ng/g wet weight, respectively, while no TTCP was detected in the chironomid sample. The concentration of TTCP in an unfiltered water sample collected in the same location and time period was 4 ng/L, indicating a BCF of 10,000 in leeches and 1,250 in Cladophora (Table 5-3).

Other studies have reported concentrations of TTCP in biota without reporting water concentrations. Thus bioconcentration factors cannot be calculated. Paasivirta et al. (1980) reported bioaccumulation of 2,3,4,6-TTCP in northern pike, clams, sponge and plankton in a contaminated Finnish lake. Tissue concentrations (fresh weight basis) were 11.1-20.2 ug/g in fish, 2.8-6.4 ug/g in clams, 1.45-6.3 ug/g in sponge and 7.95-23.1 ug/g in plankton. Environment Canada (1979b) measured concentrations of TTCP in tissues of marine crabs, mussels and staghorn sculpins near British Columbia wood preservation plants. Tissue concentrations (fresh weight basis) ranged from below detection limits to 20 ug/g in invertebrates and to 1,600 ug/g in sculpins.

Based on log P - log BCF correlations given by Neely et al. (1974), Veith et al. (1979) and Mackay (1982), and a log P value of 4.10 for 2,3,4,6-TTCP (Table 5-1), theoretical BCF's are 330-604.

Assuming a mean theoretical BCF of 514 for TTCP (Table 5-3) and using the model described by Neely (1979), an uptake rate constant of 3.0 (k_1) and a clearance rate constant of $5.9 \times 10^{-3} \text{ h}^{-1}$ are calculated for a standard trout. This clearance rate corresponds to a residence time of 169 h (ca. 7 days). While a constant clearance rate is calculated, as tissue contaminant levels become low, the rate of clearance may decline.

5.2.8 Probable Fate

Biodegradation of TTCP's in soil and in bacterial cultures has been documented; however, these compounds appear to be persistent in freshwater ecosystems, with a total environ-

mental half-life of longer than 3.5 months. Sediment enrichment of various TTCP isomers has been reported, and a high affinity for sedimentary materials is evident. Thus, sedimentation of suspended particulates contaminated with TTCP is probably a significant process for removal from the water column. Bioaccumulation factors in fish are high and depuration rates are slow relative to the lower CP's. Photolysis, chemical degradation and volatilization are probably unimportant processes for removal of TTCP from aquatic systems. Table 5-4 summarizes the aquatic fate of TTCP's.

5.3 Distribution in Ontario

Fox and Joshi (1984) measured TTCP (2,3,4,6 and 2,3,5,6) and PCP concentrations in the surface film, water column, sediments and biota in the lower Trent River and Bay of Quinte in 1978. Total TTCP concentrations were 10-1,100 ng/L in the surface film and 5-1,000 ng/L in the water column, with the highest concentrations found near the contaminant source (a wood preserving facility) in the lower Trent River and the lowest concentrations found in the lower bay. Concentrations in the water column were generally less than 100 ng/L in the bay. Surficial sediments in the bay had 5-65 ng/g dry weight, with the highest TTCP concentrations found in a silty clay sediment with high organic content. Leeches and Cladophora taken from the bay had 40 and 5 ng TTCP/g wet weight, respectively.

The Ontario Ministry of the Environment reported concentrations of 2,3,5,6-TTCP in Jackfish Bay, Lake Superior at varying distances from a pulp and paper discharge (C. Cherwinsky, Water Resources Branch, pers. comm.). Concentrations in water ranged from 0.60 ug/L near the discharge, to 0.06 ug/L 1.03 km offshore from the discharge. TTCP was below the detection limit (0.05 ug/L) at a distance of 1.53 km from the source.

Because TTCP's are breakdown products of PCP and because PCP is relatively widespread in Ontario waters receiving industrial and municipal discharges (Section 5; Jones 1981), TTCP's probably occur in waters throughout much of Ontario.

5.4 Effects on Aquatic Organisms

In general, biological effects information on tetrachlorophenols (TTCP) is more limited than for any of the other chlorophenols. This is somewhat surprising considering that

TTCP is one of the prime contaminants from wood preserving industries, and is considered more toxic than any of the lower chlorophenols. Although acute toxicity data are available for 2,3,4,6-TTCP and 2,3,5,6-TTCP, no information on chronic effects or flavour impairment potential was revealed in the course of this review. Those studies that have been conducted consist of static short-term bioassays. Relevant data on acute effects and toxicity to aquatic plants are provided in Tables 5-5 to 5-7. A summary is given in Figure 5-1 which compares measured toxicity values to existing 'safe level' standards.

5.4.1 Acute Toxicity

Bioassays conducted for 2,3,4,6-TTCP show lethal values that range from 1,510 ug/L in a 24-hour LC₁₀₀ test with lymnaeid snails (Batte et al. 1951) to 140 ug/L in a 96-hour LC₅₀ test with bluegill sunfish (Buccafusco et al. 1981; Tables 5-5 and 5-6). Primary acute values for 2,3,5,6-TTCP vary from 170 ug/L for bluegill (Buccafusco et al. 1981) to 570 ug/L for Daphnia magna (LeBlanc 1980). It is clear from these values that TTCP is probably more toxic than the lower chlorinated phenols.

5.4.2 Plant Toxicity

The U.S. EPA (1978) reported a study on the algae Chlorella pyrenoidosa in which 2,3,5,6-TTCP reduced cell production by 50% at a concentration of 2,660 ug/L. Blackman et al. (1955), using a 72-hour bioassay, found chlorosis in duckweed (Lemna minor) at a concentration of 603 ug/L 2,3,4,6-TTCP.

5.4.3 Criteria Development

The U.S. EPA (1980a) derived criteria for the protection of aquatic life by means of two approaches. The first was a maximum 'not-to-exceed' level based on acute toxicity data, and the second was a 24-hour average level based on chronic effects data. At that time, virtually no useful information on TTCP existed. A limited but sufficient amount of biological effects data has been produced recently.

Only acute data are available for 2,3,4,6- and 2,3,5,6-TTCP. The most sensitive species tested was the bluegill, with LC₅₀ values of 140 and 170 ug/L, respectively. Since no

tainting threshold data are available, the recommended criterion for TTCP is calculated based on the acute value 140 ug/L and the application factor of 0.01 for persistent toxicants, as outlined in Section 1.4, to derive a criterion of 1 ug/L.

TABLE 5-1: PHYSICAL PROPERTIES OF TETRACHLOROPHENOLS
(after Jones 1981)

CAS No.	Compound	Commercial utility	Formula	Molecular Weight	Boiling point ^a (760 mm or as stated), °C	Melting point ^a (°C)	Dissociation constant ^b at 25°C, K _a
4901513	2,3,4,5-TTCP	No	C ₆ H ₂ Cl ₄ O	231.98	sublimes	116-117	1.1x10 ⁻⁷
58902	2,3,4,6-TTCP	Yes	"	"	150(15)	70	4.2x10 ⁻⁶
935955	2,3,5,6-TTCP	No	"	"	-	115	3.3x10 ⁻⁶

Compound	pK ^{c,e}	pK ^d	Water solubility ^e (pH 5.1, 25°C) (moles/L)	Density	Vapour Pressure ^f @ °C	Log P ^g	Appearance
2,3,4,6-TTCP			7.9 x 10 ⁻⁴ (100 mg/L) ^h	-	1mm @ 100.0C	4.10	Light brown mass
2,3,5,6-TTCP	5.3						

a Weast (1974)
b Doedens (1967)
c Pearce and Simpkins (1968)
d Farquharson et al. (1958)

e Blackman et al. (1955)
f Sax (1975)
g Hansch and Leo (1979)
h Buikema et al. (1979)

TABLE 5-2a: CONCENTRATIONS (ppb) OF TETRACHLOROPHENOL IN UNFILTERED WATER, SURFACE FILM, AND SURFICIAL SEDIMENT FROM FOUR STATIONS IN THE BAY OF QUINTE (from Fox and Joshi 1984)

	Stations			
	3	4	5	6
Surface film	0.780	0.500	0.520	0.100
Water	0.030	0.010	0.010	0.005
Sediment (dry weight basis)	30	5	65	20

TABLE 5-2b: 2,3,5,6-TETRACHLOROPHENOL CONCENTRATIONS (ppb) IN FILTERED WATER AND DRY SEDIMENT IN A CONTAMINATED MISSISSIPPI LAKE (from Pierce and Victor 1978)

	Sites			
	A	B	C ^a	D
<u>PCP Spill, Dec. 1974</u>				
Aug. 11, 1976				
water ^b	0.21	0.07	0.08	0.10
sediment ^c	235	196	130	28
Oct. 22, 1976				
water	dry	0.03	0.06	0.06
sediment ^d	13	64	67	55
<u>PCP Spill, Dec. 1976</u>				
Jan. 5, 1977				
water	1.53	0.85	0.97	0.60
sediment ^d	12	97	27	24
Feb. 22, 1977				
water	1.62	-	0.25	-
sediment ^d	-	339	-	-
Apr. 27, 1977				
water	2.0	0.72	0.94	1.0
sediment ^d	3.8	71	63	24

^aAnaerobic sediment

^bAverage of triplicate values

^c Single composite sample

^d Average of duplicate values

TABLE 5-2c: CONCENTRATIONS (ppb) OF TETRACHLOROPHENOLS IN SEDIMENTS AND WATER FROM THE LOWER RHINE RIVER (Wegman and Broek 1983)

	Sediment (n = 17)			Water (n = 13)		
	Frequency (%)	Max.	Median	Frequency (%)	Max.	Median
2,3,4,5-TTCP	100	8.9	0.9	23	0.02	-
2,3,4,6-TTCP	100	4.9	1.7	92	0.20	0.07
2,3,5,6-TTCP	94	2.8	1.4	54	0.08	0.01

TABLE 5-3: BIOCONCENTRATION FACTORS AND DEPURATION RATES FOR
2,3,4,6-TETRACHLOROPHENOL AND 2,3,5,6-TETRACHLOROPHENOL
IN FRESHWATER BIOTA

	BCF	Depuration	Reference
<u>2,3,4,6-TTCP</u>			
Fish (calculated)	604		1
	609	clearance =	2
	330	$5.9 \times 10^{-3} \text{ h}^{-1}$	3,4
<u>2,3,5,6-TTCP</u>			
			5
Sunfish - muscle	<20-78	-	
- liver	40-960	-	
Bass - muscle	217	-	
- liver	4,950	-	
Catfish - muscle	53-221	-	
- liver	1,000-8,590	-	
<u>2,3,4,6 + 2,3,5,6</u>			
			6
Leech	10,000		
<u>Cladophora</u>	1,250		

¹Mackay (1982)

²Veith et al. (1982)

³Neely et al. (1974)

⁴Neely (1979) (see text for assumptions)

⁵Pierce and Victor (1978)

⁶Fox and Joshi (1984)

TABLE 5-4: SUMMARY OF AQUATIC FATE OF TETRACHLOROPHENOLS

Environmental Process	Summary Statement	Rate	Half Life	U.S. EPA's Confidence of Data
<u>Degradation Processes</u>				
Photolysis	- process apparently unreported for TTCP probably occurs to some extent; environmental relevance unknown.	-	-	low
*Biodegradation	- reported in soil and bacterial cultures; TTCP persisted in sediment and water of a contaminated Mississippi lake, suggesting slow biodegradation in aquatic systems.	-	>3.5 months	medium
Chemical Degradation	- oxidation and hydrolysis reactions are probably insignificant.	-	-	low
<u>Transport Processes</u>				
*Sorption	- probably important based on log P of 4.10 for 2,3,4,6-TTCP; sediment enrichment reported in a Mississippi lake, the Rhine River and a Finnish lake.	-	-	medium
Volatilization	- not considered important in natural surface waters.	-	-	low
Bioaccumulation	- BCF calculated from log P = 330-609 (fish); measured BCF, sunfish, bass, catfish = <20-221 (muscle), 40-8,590 (liver), leech = 10,000, <u>Cladophora</u> = 1,250	-	calculated residence time in fish 7 days	medium

Probable overall environmental half-life >3.5 months, possibly years in organic-rich sediments.

*Probable dominant processes in degradation and removal.

TABLE 5-5: PRIMARY ACUTE TOXICITY DATA FOR THE TETRACHLOROPHENOLS

Isomer Evaluated	Species	Method ¹	Test Laboratory Water Quality					Laboratory	Reference
			Individual Results (ug/L)	Geometric Mean (ug/L)	Mean pH	Mean Temp. (°C)	Hardness (as CaCO ₃ mg/L) ³		
2,3,4,6-TTCP	Cladoceran <u>Daphnia magna</u>	48 hr-LC ₅₀ S,U	290	290	8.0	22	173	E,G & G Bionomics, Mass.	LeBlanc 1980
	Bluegill <u>Lepomis macrochirus</u>	96 hr-LC ₅₀ S,U	140	140	7.2	22	40	E,G & G Bionomics Mass.	Buccafusco, et al. 1981 ^{2,3}
2,3,5,6-TTCP	Cladoceran <u>Daphnia magna</u>	48 hr-LC ₅₀ S,U	570	570	8.0	22	173	E,G & G Bionomics, Mass.	LeBlanc 1980
	Bluegill <u>Lepomis macrochirus</u>	96 hr-LC ₅₀ S,U	170	170	7.2	22	40	E,G & G Bionomics, Mass.	Buccafusco, et al. 1981 ^{2,3}

¹Terms: FT = flow-through bioassay, Semi S.= Static bioassay with solution replacement, S = static bioassay, U = test tank concentrations unmeasured, M = test tank concentrations measured, SW = water of low hardness MW = water of medium hardness, HW = water of high hardness

²Conductivity reported

³Alkalinity reported

⁴Major ions reported

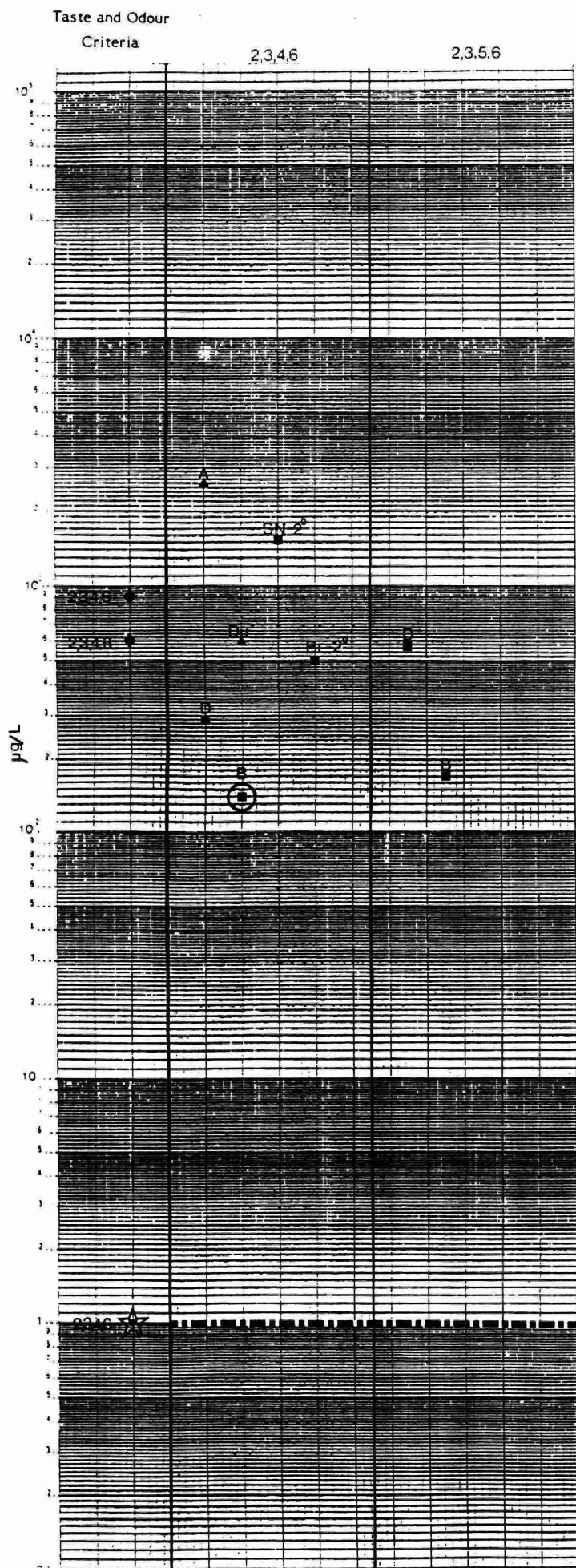
TABLE 5-6: SECONDARY ACUTE TOXICITY DATA FOR THE TETRACHLOROPHENOLS

Isomer Evaluated	Species	Method ¹	Results (ug/L)	Test Laboratory Water Quality			Laboratory	Reference
				Mean pH	Mean Temp. (°C)	Mean Hardness (as CaCO ₃ mg/L)		
2,3,4,6-TTCP	Lymnaeid Snails	24 hr-LC ₁₀₀ ,S,U	1,510	-	-	-	Florida Agric. Exp. Stn., Fla.	Batte <u>et al.</u> 1951
	<u>Brown Trout</u> <u>Salmo trutta</u>	24 hr-LC ₅₀ ,S,U	500	-	5	-	Dept. of Cell Biology, Univ. of Jyväskylä, Finland	Hattula <u>et al.</u> 1981

¹Terms: S = static bioassay, U = test tank concentrations unmeasured.

TABLE 5-7: PLANT VALUES FOR TETRACHLOROPHENOLS

Isomer Evaluated	Species	Method	Results (ug/L)	<u>Test Laboratory Water Quality</u>			Laboratory	Reference
				Mean pH	Mean Temp. (°C)	Mean Hardness (as CaCO ₃ mg/L)		
2,3,4,6- TTCP	Duckweed <u>Lemna minor</u>	Chlorosis 72hr-LC ₅₀	603	5.1	25	-	Dept. of Agric., Oxford Univ., England	Blackman <u>et al.</u> 1955
2,3,5,6- TTCP	Alga <u>Selenastrum</u> <u>capricornutum</u>	96hr-EC ₅₀ cell production	2,660	-	-	-	-	U.S. EPA 1978



CODES

- ◆ Odour Threshold
- ▼ Taste Threshold
- Acute Toxicity
- Chronic Toxicity
- ▲ Plant Data
- ★ Tainting (Fish Flesh)
- ☆ EPA Criteria
- Soviet Criteria
- 2° Secondary Data
- Recommended Criterion
- Vertical bars represent data ranges
- Critical Value in Criteria Selection

Test Species

- Du Duckweed
- A Alga
- D Daphnia
- B Bluegill
- Br Brown Trout
- SN Snails

Routine detection limits,
MOE' December 1983:
all TTCP's: 50 ng/L

FIGURE 5-1:
TETRACHLOROPHENOLS
TOXICITY AND CRITERIA SUMMARY
Recommended Criterion 1 µg/L

6.0 PENTACHLOROPHENOL

Only one isomer of pentachlorophenol (PCP) is possible, with all five substituent positions on the phenol ring occupied by chlorine atoms.

6.1 Occurrence

PCP is the most widely used CP by industry. It is available as PCP or as the sodium salt, NaPCP. PCP was manufactured in Canada (until July 1983) by:

Uniroyal Limited
Clover Bar, Alberta

and is distributed by:

Canada Colors and Chemicals Limited
160 Bloor Street E.
Toronto, Ontario M4W 1C6

Domtar Chemicals Limited
395 Maisonneuve Blvd. W.
Montreal, Quebec H3A 1L6

Bayer (Canada) Ltd.
through Dow Chemical of Canada Ltd.
P.O. Box 1012, Highway #40
Sarnia, Ontario N7T 7K1

Lawrason S.F. and Co. Limited
180 Adelaide Street S.
Box 2425
London, Ontario N6A 4G3

May and Baker (Canada) Limited
5029 Ambroise Street
Montreal, Quebec H4C 2E9

May and Baker (Canada) Limited
3300 Cote Vertu, Suite 202
St. Laurent, Montreal H4R 2B7

Van Waters and Rogers Limited
980 Van Horne Way
Richmond, B.C. V6X 1W5

Harrisons and Crosfield (Canada) Limited
4 Banigan Drive
Toronto, Ontario M4H 1G1

Kingsley and Keith (Canada) Limited
310 Victoria Ave.
Montreal, Quebec H3Z 2M9

Reichhold Chemicals Limited
P.O. Box 130
Port Moody, B.C. V3H 1E1

PCP, often in combination with TTCP, is an active ingredient in wood preservatives. Water-soluble NaPCP is also widely used in water treatment, in leather and tanning industries, in fungicides, and in various other industrial sectors (Jones 1981). A total of 1,928,300 kg of PCP (including NaPCP) were used in Canada in 1976 (Jones 1981).

Biocides containing PCP may contain the toxic impurities polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) (Jones 1981). The environmental behaviour and toxicology of these impurities will not be discussed in this report.

Forest products industries appear to be the major source of PCP to the environment. Shields (1976) described engineering processes and treatment systems that are probable sources of PCP contamination from wood processing plants. Unfortunately, their wastewaters are usually described according only to phenol content, with effluent rarely

analyzed for concentrations of CP's including PCP. Surface wood treatment at sawmills and lumber export terminals also uses PCP, and facilities pose environmental hazards when inadequately designed and operated (Jones 1981). Groundwater contamination by PCP was reported at a wood preservation industry at Thunder Bay. Contaminated groundwater contained 2.05 to 3.35 mg/L PCP (Thompson et al. 1978). Environment Canada (1977a) observed PCP in laboratory-prepared bleach effluents from softwood and pulping processes. The Ontario Ministry of the Environment reported PCP in Jackfish Bay, Lake Superior near a pulp and paper discharge (C. Cherwinsky, Water Resources Branch, pers. comm.). PCP contamination was reported in the lower Trent River and Bay of Quinte, Ontario, downstream from a wood preserving facility (Fox and Joshi 1984).

PCP generally occurs in effluents from sewage treatment plants. Fox (1978) reported 65 to 1,300 ng/L of PCP in 13 effluent samples from 7 sewage treatment facilities in southern Ontario. Garrett (1980) reported PCP levels in sewage effluents from Greater Vancouver. Arsenault (1976) reported that the addition of 10 mg/L of chlorine to 1 mg/L of phenol can generate 0.2 ug/L of PCP, indicating that some PCP may be formed by sewage treatment processes.

Agricultural and domestic use of PCP may provide a minor, diffuse source to surface water systems. As summarized by Jones (1981), commercial PCP/TTCP preparations are used in agriculture to prevent wood decay in farm buildings, fences, etc. Commercial PCP may also be used in combination with herbicides in weed control. In domestic use, PCP is found wood treatment preparations for home-owners and in some dental care products (Jones 1981).

Wastes from other industries and from landfill sites may include PCP. Garrett (1980) reported PCP in various landfill leachates and discharges in Greater Vancouver. However, no PCP was reported in surface waters draining hazardous chemical landfills in Niagara Falls, New York (Elder et al. 1981).

PCP may be transported widely in the atmosphere, resulting in contamination of surface waters in remote areas. Snow samples collected in winter 1977-78 in Ontario showed PCP contamination at levels of <0.001-0.003 ug/L in meltwater at 8 of 19 sites (Strachan 1979a). PCP was observed in snow from Point Pelee to the Hearst and Timmins areas.

6.2 Environmental Fate

6.2.1 Physical and Chemical Properties

A summary of the physicochemical properties of PCP is presented in Table 6-1 and 6-2. These properties control the behaviour of PCP in surface water systems.

The log octanol-water distribution coefficient of PCP is high ($\log P=5.01$; Table 6-1). Kaiser and Valdmanis (1982) showed that $\log P$ for PCP is highly pH-dependent, with apparent $\log P$ values of 4.84 to 4.5 at pH 1 to pH 5. As pH rose from 5.9 to 8.9, $\log P$ fell from 3.72 to 2.75, presumably due to ionization of this weak acid (pK_a 4.8). At pH 9.3 to 12.5, $\log P$ values were 1.30 to 2.42. Increases in $\log P$ were then observed at pH 13.5. $\log P$ values reported in the literature (i.e. 5.01) are based on an ion-corrected partition coefficient. Kaiser and Valdmanis (1982) pointed out that bioconcentration and sorption of PCP correlate with the effective or apparent $\log P$ values rather than with the ion-corrected $\log P$. Thus, the environmental behaviour of PCP will depend strongly on pH and on ionic properties of both effluents and receiving waters.

6.2.2 Photolysis

Several studies have demonstrated the photolytic breakdown of PCP. Kuwahara et al. (1966) observed that the photochemical degradation of NaPCP in aqueous solution led to the formation of various products, primarily chloranilic acid and a yellow compound identified as complex molecule of $C_{12}H_4O_4Cl_7$. The photodegradation products of NaPCP identified by Munakata and Kuwahara (1969) showed stronger fungicidal activity but lower toxicity to plants and fish than PCP. Crosby and Hamadmad (1971) irradiated PCP in various organic solvents but observed only one photodegradation product - 2,3,5,6-TTCP. They felt that photolysis of PCP probably has little significance in loss from the environment. A reaction scheme for photolysis of PCP leading to various TCP's, trichlorodiolis and small fragments including CO_2 and HCl was described by Wong and Crosby (1981). A review of photodegradation products of PCP was provided by Jones (1981).

PCP appears to be subject to photolysis under environmental conditions. Fox and Joshi (1984) reported that photodegradation of PCP appeared to account for increasing TTCP:PCP ratios with downstream distance from the contamination source in the lower

Trent River and Bay of Quinte. The TTCP:PCP ratio in the surface film (where light energy levels are highest) exceeded those found in the water column, strongly suggesting photochemical dechlorination. Boyle et al. (1980) studied the degradation of PCP in simulated lentic environments in aquaria. Light, high pH and high dissolved oxygen content were associated with the most rapid breakdown of PCP. In a study examining photolytic rates at different pH, Wong and Crosby (1981) reported similar rates of photolysis in laboratory solution and in rice-field water. Pierce and Victor (1978) attributed the origin of two major degradation products-2,3,5,6-and 2,3,4,5-TTCP - to photolytic dechlorination of PCP held in a waste treatment pond.

Rates of photolysis have been described in the literature and were used by NRCC (1982) to predict photolysis rates in the environment. Hiatt et al. (1960) found that 10 mg/L of NaPCP was degraded by 290-330 nm wavelength light at $3.4 \times 10^{-4} \text{ s}^{-1}$ (pH 7). Photolytic rates were described by Wong and Crosby (1978) as $5.2 \times 10^{-7} \text{ s}^{-1}$ at pH 3 and $2.7 \times 10^{-5} \text{ s}^{-1}$ at pH 7. These pH's correspond to proportions of ionized PCP of 1% and 99%, respectively. Data provided by Wong and Crosby (1981) indicate half-lives ($T_{1/2}$) due to photolysis of about 4 h at pH 7.3 and 100 h at pH 3.3. Using the data of Hiatt et al. (1960) and Wong and Crosby (1978) and the absorption spectrum described by Lang (1965) and Fountaine et al. (1975), NRCC (1981) estimated photolysis rates for PCP in winter and summer for highly-polluted waters in Canada:

<u>Latitude</u>	<u>Month</u>	<u>$T_{1/2}$</u>	
		<u>pH 7</u>	<u>pH 3-4</u>
45° N	June	57 min	4.6 d
	Dec	5.1 h	49.5 d
50° N	June	57 min	4.9 d
	Dec	8 h	99.0 d
60° N	June	59 min	5.3 d
	Dec	1.8 d	175 d

The predictions of NRCC (1982) apply to water surfaces. A depth of 1 m has the same effect as both a four unit pH reduction and the difference between the extremes of attenuation, making depth the controlling factor for photolysis in the environment. For a

1 m deep polluted aquatic system at 45° N in June, the rate constant would be 0.175 d⁻¹ and T_{1/2} would be 4 d (NRCC 1982). From these considerations, it would seem that photolysis is relatively rapid (T_{1/2} = hours to days) in clear, relatively shallow waters at neutral pH (e.g. rivers, shallow lakes). In turbid or deep waters at low pH, photolysis becomes increasingly slow (T_{1/2} of many weeks or months).

6.2.3 Microbial Degradation

While most studies of microbial degradation of PCP have concerned soil bacteria and bacterial cultures, several studies have specifically addressed biodegradation in aquatic systems.

Boyle et al. (1980) investigated the disappearance of PCP in dark and illuminated aquaria containing pond water and sediment under both aerobic and anaerobic conditions. The half-life of PCP ranged from 12.8 to 79.8 days, with the shortest T_{1/2} occurring in illuminated aerobic conditions. Loss of PCP and formation of pentachloroanisole was considered to be enhanced by photolysis and by aerobic bacteria.

In an investigation of PCP breakdown by sewage sludge bacteria under aerobic and anaerobic conditions, Liu et al. (1981) similarly reported the shortest T_{1/2} under aerobic conditions. Half-lives in aerobic and anaerobic conditions were 0.36 and 192 days, respectively. The authors noted that low oxygen conditions in sediments and thus, low rates of microbial degradation may in part account for high PCP levels in sediments relative to those in the water column in the natural environment. The addition of other organic compounds and contaminants and different forms of nitrogen to the cultures had varying stimulatory or inhibitory effects on PCP biodegradation rates.

Trevors (1982) examined the effects of temperature on degradation of PCP by Pseudomonas cultures isolated from stream water and soil. Half lives were at least 80 days at 4°C and 8 - 10 days at 20 °C. No degradation was observed at 0°C.

An investigation of PCP breakdown in natural sediment showed slow rates of loss by microbial action (Baker et al. 1980). Only a 12% loss of PCP was reported in 30 days. This observation may support the conclusion of Liu et al. (1981) that PCP degradation is probably slow in sediments due to low oxygen tension.

Fox and Joshi (1984) measured concentrations of PCP in various ecosystem components at the mouth of the Trent River and throughout the Bay of Quinte (Ontario) downstream of a wood preserving plant. In a sediment core collected from a relatively deep area of the bay, concentrations of TTCP and PCP decreased gradually with depth. This suggested either slow degradation or increasing loadings of wood preservatives over time. The authors noted that a remarkably constant TTCP:PCP ratio with depth in the core suggested increased loading and not degradation was responsible for the concentration change. A depositional period of 30 years was sampled in the core, suggesting that these compounds are highly resistant to biodegradation in this environment. These sediments were relatively rich in organic matter and may have been anaerobic, resulting in poor conditions for biodegradation. If biodegradation was responsible for the decline in concentration with time, the half-life for removal by this process would appear to be in the order of five to ten years.

In their study of PCP in a small Mississippi lake following accidental chemical spills, Pierce and Victor (1978) identified the major PCP breakdown products of 2,3,4,6-TTCP and pentachloroanisole in water, sediment and fish tissue. Decomposition of PCP was attributed to photolysis and to microbial activity. Concentrations in water and in sediment declined between January 5, 1977 immediately after a spill and April 27, 1977. However, rates of decomposition cannot be readily estimated from the data due to the probable importance of other removal processes such as sedimentation, downstream transport, and photolysis.

Kreuk and Hanstveit (1981) added 1 mg/L of PCP and bacteria to a freshwater nutrient medium and to seawater. Seventy percent degradation was achieved in 75 to 90 days in the freshwater medium. In seawater tests, results were more variable with no degradation observed in one experiment and 70% degradation after 45 days in another.

Studies on degradation of PCP in sewage treatment systems have shown conflicting results. Pauli and Franke (1972) observed no removal of PCP in sewage after 14 days. Conversely, in a demonstration of the biological treatment of PCP in a sewage treatment plant, mixtures of PCP in aeration lagoon influent were continuously aerated and analyzed (Arsenault 1976). In two experiments reported by Arsenault (1976), PCP concentrations fell from 39.5 ppm to 0.5 ppm in three days and from 81 ppm to 0.6 ppm in 30 h.

Several studies have demonstrated the ability of cultured soil microorganisms to metabolize PCP. Chu and Kirsch (1972) and Kirsch and Etzel (1973) reported oxidation of PCP by cultured bacteria. Kirsch and Etzel (1973) also found that when alternate carbon sources were provided in combination with PCP, PCP is degraded much more slowly. A Gram-variable bacillus was grown on PCP as the sole carbon source and was reported to mineralize the compound to CO_2 and Cl^- (Chu 1972). Watanabe (1973) reported that acclimated Pseudomonas grown in 40 ppm PCP was able to remove the chlorine atoms from PCP molecules within about three weeks. Of seven species of fungi studied by Cserjesi (1967), two Trichoderma species were capable of degrading 10 ppm PCP. Using C-14 labelled PCP, Suzuki (1977) observed rapid degradation of PCP to CO_2 by Pseudomonas and incorporation of C-14 into cellular constituents. While the majority of studies have clearly demonstrated PCP degradation by microbial cultures, Vela-Muzquiz and Kasper (1973) reported the inability of various cultured soil bacteria to degrade PCP or NaPCP when supplied as the only carbon source.

When PCP is applied to agricultural systems, soil microorganisms have been found to adapt accordingly. Watanabe (1977) observed the responses of natural bacteria to PCP application in upland Japanese rice fields. Populations of PCP-tolerant and PCP-decomposing bacteria increased immediately following application of the chemical. These results suggest that microbial degradation of PCP occurs in natural soils as well as under laboratory culture conditions.

A few authors have proposed chemical pathway schemes for microbial metabolism of PCP. Reiner et al. (1978) proposed a hypothetical pathway for degradation with successive dechlorinations and production of various quinone intermediates. Rott et al. (1979) identified a total of 10 metabolites of NaPCP in soil bacteria cultures with PCP-acetate being the most predominant. As mentioned previously, removal of chlorine atoms and production of CO_2 and organic cellular constituents from PCP have been observed in bacterial culture tests (Chu 1972; Watanabe 1973; Suzuki 1977). A review of PCP breakdown schemes was provided by Jones (1981).

Although NRCC (1982) felt that biodegradation is probably not a significant process for removal of PCP from surface waters, evidence for the occurrence of microbial metabolism of PCP in nature is strong. While information on the relative importance of microorganisms in the removal of PCP is somewhat conflicting, most studies relevant to

aquatic systems support a half-life for biodegradation in the order of 100 days, with higher temperatures and aerobic conditions favouring more rapid breakdown. PCP may persist for years in sediments.

6.2.4 Chemical Degradation

Data on abiotic chemical processes affecting the fate of PCP in water and soil are sparse. Strufe (1968) reviewed the role of stream velocity and water quality on NaPCP. It was determined that various inorganic salts (e.g. iron, lead, copper) may deactivate NaPCP by the formation of insoluble complexes. For example, in water with a very high iron content of 30 mg/L, the concentration of NaPCP declined progressively from 10 mg/L to 2 mg/L in 120 days. Pierce and Victor (1978) identified 2,3,5,6 -TTCP, 2,3,4,5-TTCP, pentachloroanisole and anisoles of both TTCP isomers in a lake following PCP spills. However, the significance of strictly chemical processes in these transformations is unknown. The authors felt that photolysis and microbial degradation were probably the primary controlling factors. Chemical degradation of PCP in soils is presumed to be caused and promoted by microbial action (Kuwatsuka 1972).

According to Morrison and Boyd (1973), highly chlorinated compounds are usually resistant to oxidation at environmental temperatures. While the U.S. EPA (1979) concluded that oxidation of PCP is probably insignificant in aquatic systems, NRCC (1982) felt that the process of oxidation in CPs deserves reexamination. Hydrolysis of PCP in the environment is likely an unimportant process because of the resistance of substituents attached to an aromatic ring to hydrolytic reactions.

6.2.5 Sorption Processes

The ion-corrected log P of PCP is very high relative to lower CPs (5.01; Table 5-1). As discussed earlier (Section 5.2.1), effective log P values are highly dependent on pH and on ionic properties of the medium. High log P values indicate a high potential for accumulation by particulates with high organic content (Karickhoff et al. 1979). Because log P values are highest under acidic conditions (pH 5), sorption is expected to be most pronounced at low pH. Nitka et al. (1982) studied the sorption-desorption of PCP in pulpwood fibres and as predicted by log P values, PCP was strongly bound to fibres at low pH but was largely mobilized into solution at neutral pH in process streams.

Table 6-3a shows concentrations of PCP in surface film, unfiltered water and sediment from the Bay of Quinte, downstream of a wood preserving facility (Fox and Joshi 1984). Sediments were enriched with PCP by factors of 46-390 with respect to concentrations found in the surface film. Enrichment factors in sediment with respect to concentrations in water were 960-3,600, excluding data from one station where no PCP was detected in the water column.

Table 6-3b shows PCP concentrations in sediment and filtered water in a small Mississippi lake (Pierce and Victor 1978). PCP spills occurred in December 1974 and December 1976. The data indicate high concentrations in sediment relative to water before the 1976 spill (sediment-water distribution coefficient 212 - >3300). Following the spill, dissolved PCP levels rose by one to two orders of magnitude while sediment PCP levels remained relatively unchanged. A gradual decline in dissolved PCP was observed from January 5 to April 27, apparently due to processes such as sorption and sedimentation, photolysis, microbial breakdown and downstream transport. The rate of decline shown by these data suggest an environmental half-life of less than 3.5 months.

Wegman and Broek (1983) measured water and sediment concentrations of PCP in the lower Rhine River. Water samples were apparently unfiltered. PCP was identified in all of 17 sediment samples and 13 water samples collected. The median concentration in sediment was 8.4 ug/kg dry weight and in water was 0.41 ug/L, indicating a sediment-water distribution coefficient of 20.

In contaminated Finnish lakes, Paasivirta et al. (1980) reported mean PCP levels of 33.4 to 50.1 ug/kg dry weight in sediments. Although PCP concentrations in water were not determined, these relatively high concentrations in sediment are suggestive of a sedimentary sink.

Sorption of PCP in particulates has received considerable attention. As postulated for aquatic sediments (Kaiser and Valdmanis 1982), PCP is more strongly bound to soil particles under acidic conditions than under alkaline conditions, and the adsorption coefficient is also positively correlated with organic content and cation exchange capacity. A review of sediment sorption properties of PCP is provided by Jones (1981).

NRCC (1982) derived a predictive model to describe the sorption of unionized PCP in aquatic systems. Ionization of PCP is pH dependent. The ionized form was considered not to sorb onto particulates. Partitioning was expressed as a function of organic carbon content and the correlation between the organic carbon:water partition coefficient and log P, as described by Karickhoff et al. (1979). A PCP adsorption rate of 1 - 100 g water.g sediment⁻¹.day⁻¹ was estimated for surface waters in general.

From these studies, it is evident that PCP accumulates in sediments in the aquatic environment. While the nature of the sorption process is unclear (NRCC 1982), acidity and organic content obviously play a key role. Also, as discussed in Section 6.2.3, inhibition of PCP degradation in anaerobic conditions may favour the accumulation and persistence of this compound in anoxic sediments.

6.2.6 Volatilization

Klopffer et al. (1982) studied volatilization of PCP in water with controlled "wind" conditions (air velocities). Volatility was found to decrease sharply with increasing pH due to the greater dissociation of PCP at higher pH. Thus, at pH 8, no volatilization was observed. Half-life in the laboratory solution declined from 3,120 h at pH 6 to 151 h at pH 4. Volatilization was independent of wind velocities at 1 m.s⁻¹, but was a function of temperature, water solubility, vapour pressure, solution mixing depth, and molar mass of the chemical. Assuming volatilization of 1 ug/L PCP from a sluggish river and a wind speed of 5 m.s⁻¹, a theoretical flux to air of 4×10^{-13} kg · m⁻².s⁻¹ was calculated.

NRCC (1982) derived rate constants for volatilization of PCP from water. Solubility of the undissociated form susceptible to volatilization was assumed not to change with pH. Based on estimates of solubility and vapour pressure estimated for liquid and crystalline PCP, volatilization rates of 1.7×10^{-2} cm.day⁻¹ and 1.4×10^{-1} cm.day⁻¹ were calculated. NRCC (1982) also noted that the work of Wong (1978) and Kilzer et al. (1979) indicated that PCP volatilizes at higher pH (pH > 7) for unexplained reasons. This is contrary to the observation of Klopffer et al. (1982) that PCP does not readily volatilize at pH 8.

The U.S. EPA (1979) stated that compounds such as PCP with moderate solubility in water and a low vapour pressure do not readily volatilize from water. Furthermore, they

stated that PCP in surface waters will be dissociated to varying degrees, depending on pH, and that ionized PCP is not volatile.

Information provided by Klopffer et al. (1982) suggests that volatilization may be a removal process of some importance for PCP in surface waters, particularly in well mixed, shallow water at low pH (<5). At pH levels greater than 6, observed half-lives were long ($T_{1/2} > 130$ days) in shallow, laboratory systems. As pH approaches 8 in surface waters, volatilization probably ceases (Klopffer et al. 1982) or proceeds at a slow rate for unexplained reasons (Wong 1978; Kilzer et al. 1979).

6.2.7 Bioaccumulation

Several studies of bioaccumulation of PCP by freshwater biota have been reported. The reader is referred to the review of Jones (1981) for information on uptake in marine organisms. Data on bioaccumulation in freshwater biota are summarized in Table 6-4.

Fox and Joshi (1984) reported PCP concentrations in biota from the Bay of Quinte, downstream from a source of PCP contamination. Based on a PCP concentration in unfiltered water of 17 ng/L at the same location, bioconcentration factors (BCF's) were 60-5,000 in invertebrates, 9,100-15,000 in fish and 400 in Cladophora (Table 6-4).

Pierce and Victor (1978) measured concentrations of PCP, TTCP and breakdown products (anisoles) in a small Mississippi lake following two accidental spills. Concentrations of PCP were measured in muscle and liver of sunfish, bass and catfish. Concentrations of PCP in filtered water samples were also measured. Mean concentrations in water for October 1976 before the December 1976 spill, in January 1977 and April 1977 were <0.5, 37 and 88 ug/L, respectively. Mean concentrations and ranges in fish tissues (ng/g fresh weight) during the same months were:

	<u>Sunfish</u>		<u>Bass</u>		<u>Catfish</u>	
	Muscle	Liver	Muscle	Liver	Muscle	Liver
October 1976	4.5 (4-5)	88 (26-150)	-	-	-	-
January 1977	7,900 (6,400-9,400)	130,000	13,000 (7,000-17,000)	222,000 (14,000-325,000)	19,000	214,000
April 1977	950 (900-1,000)	14,850 (14,600-14,900)	-	-	4,850 (1,500-8,200)	35,400 (20,200-50,600)

From these mean fish tissue and water concentrations, BCF's of $>9 - 514$ for muscle tissue and $176 - 6000$ for liver are calculated, as detailed in Table 6-4. The highest tissue concentrations were observed in bass and catfish. The appearance of pentachloroanisole (PCP - OCH_3) in fish tissues was attributed to conversion from PCP by gut microflora, by direct uptake from water or by food chain transport.

Goldfish (Carassius auratus) exposed to 0.1 mg/L of PCP for 120 h had a BCF of about 1000 (Kobayashi and Akitake 1975). The rate of bioaccumulation was higher at higher PCP concentrations. The highest tissue concentrations were observed in gall bladder. When transferred to water, depuration was rapid with losses of 50% and 80% of the total body burden in 10 and 20 h, respectively. The remaining 20% was eliminated more slowly.

Trujillo et al. (1982) measured uptake and clearance of PCP in killifish (Fundulus similis) exposed to 57 to 610 ug/L. The maximum body burden of PCP was reached after about five days with a BCF of 53. The half-life for bioaccumulation was about 25 h. The $T_{1/2}$ for depuration in clean water was 4.7 days, with clearance initially rapid and then declining after four days. The authors noted that conversion of some of the PCP to PCP- OCH_3 in fish or in the aquaria may have reduced the depuration rate.

Relatively large (400 g) rainbow trout (Salmo gairdneri) were exposed to 10 (control), 35 and 660 ng/L NaPCP in circulating water (Niimi and McFadden 1982). PCP concentrations were controlled with continuous infusion of the chemical. Fish accumulated PCP according to concentrations in water and duration of exposure. Concentrations of PCP in "tissue" (whole fish minus liver and gall bladder) and "organ" (liver and gall bladder) increased with time over the 115 day duration of the experiment. Niimi and McFadden (1982) estimated BCF values of 200 and 240 at the low and high exposure levels, respectively.

Freitag et al. (1982) studied the uptake of several organic chemicals including PCP in aquatic biota. A BCF of 1250 was observed in Chlorella fusca exposed to 50 ug/L over 24 h. In golden orfe (Leuciscus idus melanotus) exposed to 42 ug/L for three days, a BCF of 1140 was reported.

Pruitt et al (1977) exposed bluegill (Lepomis macrochirus) to 0.1 mg/L PCP. Bioconcentration factors in various tissues ranged from 10 to 350. The highest BCF was reported in liver, followed by digestive tract tissue, gills and muscle. When fish were returned to clean water, depuration was rapid although low concentrations of residues persisted after 16 days.

Fox and Hodson (1978) reported the preliminary results of exposure of an experimental ecosystem to PCP. The BCF for various biota was reported as 100 times the concentration in water (Jones 1981).

In an earlier study, Ahling and Jernelov (1969) estimated the $T_{1/2}$ for PCP in guppies (Poecilia reticulata) at 30 days. This result is quite high in relation to others reported in the literature.

In an examination of relationships between physicochemical properties of phenolic compounds and accumulation in fish, Saarikoski and Viluksela (1982) reported a BCF of about 500 in guppies. Exposure concentrations were described as "sublethal" and the pH of test solutions was maintained at 6. The authors predicted a BCF of 1300 for PCP based on a log P value corrected for ionization.

In Veith et al.'s (1979) derivation of a log BCF -log P correlation, an experimental BCF of 770 for fathead minnow (Pimephales promelas) was measured. This contrasted with their much higher predicted BCF of about 4,900.

NRCC (1982) used metabolic rate functions, a log P of 3.80 for PCP, and data on clearance of chemicals from fish (Neely et al. 1974) corrected for lipid content, growth and body weight to estimate a BCF of 340. Rates of uptake and clearance were predicted at 2.9×10^1 and $8.6 \times 10^{-2} \text{ g}^{0.2} \cdot \text{d}^{-1}$, respectively. However, it was noted that these values are much lower than clearance rates provided in the literature, because dissociated PCP does not fit standard models for bioaccumulation of lipophilic compounds. The log P value used here appears to be the apparent log P at about pH 7, based on the log P-pH relationships for PCP described by Kaiser and Valdmanis (1982).

Theoretical BCFs may be calculated based on octanol:water partition coefficients - BCF correlations described by Neely et al. (1974), Veith et al. (1979) and Mackay (1982). Veith et al. (1979) and Mackay (1982) calculated BCF values for PCP in fish using a log P of 5.01 (for undissociated PCP), and derived BCFs that were considerably higher than those measured in fathead minnows. Kaiser and Valdmanis (1982) showed that log P for PCP is highly dependent on pH due to its dissociation characteristics. A log P of 3.80 for PCP was used for BCF calculations by NRCC (1982). Using a log P of 5.01, the calculated BCFs for fish range from 1120 - 4910 (Table 6-4). Based on the log P of 3.80, the calculated BCF is 220 to 340 (Table 6-4).

Assuming a mean theoretical BCF of 3,220 based on a log P of 5.01 and using the uptake-clearance model given by Neely (1979), an uptake rate constant of 3.8 (k_1) and a clearance rate constant of $1.2 \times 10^{-3} \text{ h}^{-1}$ are calculated. This clearance rate corresponds to a residence time of 856 h (36 days). Substituting the log P of 3.80 and the mean theoretical BCF of 287 based on this log P for undissociated PCP, an uptake rate constant of 2.8 (k_1) and a clearance rate of $9.7 \times 10^{-3} \text{ h}^{-1}$ are calculated. From this latter clearance rate, a residence time of 103 h (4.3 days) is determined. While constant clearance rates are calculated, depuration may become diminished as tissue contaminant levels reach low levels. The study of Kobayashi and Akitake (1975) described previously provides evidence to support this hypothesis.

6.2.8 Probable Fate

Biodegradation of PCP has been observed in water, soil and bacterial culture systems. Information on its relative importance in the environment is conflicting, but most studies would indicate a $T_{1/2}$ for degradation of <100 days, with higher temperatures and aerobic conditions favouring biodegradation. Bioaccumulation factors/bioconcentration factors are relatively high in freshwater biota but depuration rates appear to be rapid. Sediment enrichment of PCP has been observed, and sedimentation of suspended particulates is probably an important process for removal of PCP from water. Photolysis may also be significant, particularly in shallow, clear surface waters. Volatilization probably also contributes somewhat to the removal of PCP from well-mixed surface waters at low pH. Chemical degradation processes without microbial mediation are of uncertain but probable low importance in surface water systems. Table 5-5 summarizes the aquatic fate of PCP.

6.3 Distribution in Ontario

Information concerning the occurrence and distribution of PCP in Ontario was summarized by Jones (1981), primarily from data collected in an extensive survey by the Canada Centre for Inland Waters in 1977. Maps illustrating the extensive distribution of PCP around the Canadian shoreline of the Great Lakes were provided by Jones (1981). Results were summarized by Fox (1978) as follows:

"In 1977, 85 whole bulk water samples from stream mouths, nearshore areas adjacent to stream mouths and interconnecting rivers and channels on the Canadian shores of the Great Lakes were analyzed for pentachlorophenol. Levels of pentachlorophenol ranging from <5 ng/L to 1400 ng/L (with transient highs of up to 23,000 ng/L after periods of heavy rainfall) were observed. Only 8 sites produced samples with no detectable pentachlorophenol. The highest levels occurred in watersheds along the Lake Erie and Lake Ontario shorelines.

"Thirteen sewage effluent samples from 7 treatment plants in southern Ontario were also analyzed for pentachlorophenol which was observed in all samples, ranging from 65 ng/L to 1,300 ng/L."

Fox and Joshi (1984) measured PCP and TTCP concentrations in the surface film, water column, sediments and biota in the lower Trent River and Bay of Quinte in 1978. Total PCP concentrations were 10-5,809 ng/L in the surface film, and <2-5,690 ng/L in the water column, with the highest concentrations found near the contaminant source (a wood preserving facility) in the lower Trent River and the lowest concentrations found in the lower bay. Concentrations in the water column were usually less than 50 ng/L in the bay. Surficial sediments in the bay had 21-86 ng/g dry weight. PCP concentrations (ng/g wet weight basis) in organisms taken from the bay were 155-260 in fish, 1 in chironomids, 85 in leeches and 7 in Cladophora.

Water samples were collected in June 1978 for PCP analysis from the Thunder Bay, Marathon and Michipicoten areas of Lake Superior (Strachan 1979). The average PCP level at Thunder Bay and Marathon was 11.0 ug/L and at Michipicoten it was 29.0 ug/L.

The Ontario Ministry of the Environment reported concentrations of PCP in Jackfish Bay, Lake Superior near a pulp and paper discharge (C. Cherwinsky, Water Resources Branch, pers. comm.). Concentrations in water ranged from 0.540 ug/L near the discharge to 0.065 ug/L 1.03 km offshore from the discharge. PCP levels were below the detection limit of 0.05 ug/L at a distance of 1.53 km from the source.

PCP was detected in groundwater from a wood treatment facility at Thunder Bay (Thompson et al 1978). Concentrations in samples ranged from 2.05 to 3.35 mg/L.

Strachan (1979) reported concentrations of PCP in snow samples from 19 locations in Ontario during the winter of 1977 - 78. Snow melt contained <0.001 to 0.003 ug/L at 8 of the sites. Many of the sites which were positive for PCP were relatively remote from PCP sources, and ranged from Point Pelee National Park in extreme southwestern Ontario to Kettle Lake Provincial Park near Timmins and Fushimi Lake Provincial Park near Hearst. This study provided evidence that PCP is transported atmospherically.

6.4 Effects on Aquatic Organisms

PCP is thought to be the most toxic of the chlorinated phenols as reflected by the degree of chlorination. There is an abundance of information on biological effects of PCP - more than for any of the other chlorophenols.

The quality of toxicity information on PCP is generally better than that found for the other CP isomers. Approximately 45% of the acute values considered in this review were derived from flow-through bioassays in which toxicant concentrations were measured in the test vessels.

PCP, a prime biocide ingredient, usually contains various chemical impurities which are more prevalent in technical grade than laboratory grade material. The majority of these impurities consist of lower chlorinated phenols (TCP and TTCP) as well as molecular condensation products (dibenzo-p-dioxins, dibenzofurans and diphenylethers) (U.S. EPA 1980d). The contribution of these impurities to the toxicity of PCP is difficult to assess. Because of their low concentrations, chemical impurities would have to show toxic levels several orders of magnitude greater than that of PCP to significantly influence toxicity.

Relevant acute and chronic effects data are given in Tables 6-6 to 6-10. The more useful toxicity levels are summarized and compared to various regulatory standards in Figure 6-1.

6.4.1 Acute Toxicity

The large amount of primary acute toxicity data available for PCP allows reasonably accurate estimates of the effects on a wide range of fish and invertebrates (Table 6-6). Warmwater fish species, such as goldfish, fathead minnows and channel catfish, showed LC_{50} values that ranged from 50 ug/L to 600 ug/L. More sensitive warmwater species such as bluegill produced LC_{50} 's ranging from 20 ug/L to 305 ug/L. Coldwater game fish such as rainbow trout, various species of salmon and brook trout showed acute toxicity effect levels of from 34 ug/L to 220 ug/L. Sensitive invertebrates, including lymnaeid snails and species of Daphnia, showed LC_{50} values that ranged from 240 ug/L to 2,000 ug/L. Oligochaetes, in numerous bioassays with PCP, ranged in LC_{50} value from 259 ug/L to 970 ug/L. These data would suggest that invertebrates are somewhat less sensitive to PCP than fish. Further, it is clear that PCP is generally more toxic than any of the lower chlorophenols.

According to research conducted by Saarikoski and Viluksela (1982), PCP is less toxic in alkaline waters. Because of dissociation in slightly acid water, toxicity tends to decrease

with increasing pH. The effect of pH on invertebrate and fish toxicity of PCP has also been shown by Whitley (1968) and Davis and Hoos (1975).

In addition to acute toxicity demonstrated in the laboratory, PCP and TTCP have been associated with fish kills. In British Columbia between 1960 and 1973, four kills were related to wastewater from the treatment of wood (Mackenzie et al. 1975). Apparently there is no information on kills in Ontario related to PCP.

6.4.2 Chronic Toxicity

Less work has been carried out to establish the chronic effects of PCP on aquatic organisms (Tables 6-8 and 6-9). However, the available data are ample for the purposes of criteria development. The majority of meaningful studies consist of life cycle or early life stage bioassays on fish and invertebrates.

The most critical response was recorded by Webb and Brett (1973) in which sockeye salmon were exposed to PCP at concentrations ranging from 1.05 to 43.60 ug/L for eight weeks. Growth rates and food conversion efficiency were measured and threshold concentration values were calculated to be 1.61 and 1.66 ug/L, respectively. The highest observed no-effect level was 1.84 ug/L for the growth response. In another study, Hodson and Blunt (1981) using a 28-day early life stage bioassay on rainbow trout, observed chronic effects at 11 ug/L. It was also found that increasing temperature from 5.4°C to 20.1°C enhanced the effects of PCP on growth rates.

On the basis of the most commonly considered endpoints of chronic toxicity, including chronic mortality, reproduction, and growth rate, it would appear that coldwater game fish such as rainbow trout, salmon and brook trout are the most sensitive to PCP, with effect levels ranging from 1.74 to 213 ug/L. Warmwater fish species including fathead minnows, goldfish and guppies were chronically affected at PCP concentrations ranging from 45 ug/L to 462 ug/L. Sensitive invertebrates such as Daphnia magna showed 21-day LC₅₀ values ranging from 180 ug/L to 400 ug/L.

6.4.3 Plant Toxicity

Huang and Gloyna (1968) studied the effect of PCP and 40 other substituted phenols and herbicides on chlorophyll destruction and photosynthetic inhibition in the unicellular green alga, Chlorella pyrenoidosa. PCP was by far the most toxic compound tested, producing complete destruction of chlorophyll in 72 hours at 7.5 ug/L. However, during PCP toxicity studies on the same algal species, Adema and Vink (1981) recorded the 96-hour EC₅₀ (growth inhibition) for C. pyrenoidosa as 7,000 ug/L. This represents a difference of almost three orders of magnitude between results on the same algal species. Adema and Vink (1981) also exposed the alga, Scenedesmus quadricauda, to PCP and observed a 96-hour EC₅₀ of 80 ug/L for growth inhibition. Palmer and Maloney (1955) exposed blue-green algae, green algae and diatoms to PCP over 3 to 7-day periods; toxicity was observed at 1,800 ug/L in all species.

Two macrophytes have been subjected to PCP exposure - the water hyacinth (Crassipes eichornia) and the duckweed (Lemna minor). Toxic effects were seen at 4,600 and 800 ug/L, respectively.

6.4.4 Flavour Impairment

Shumway and Palensky (1973) attempted to establish a tainting threshold for PCP in rainbow trout. However, they found that PCP was acutely toxic before a tainting threshold was reached.

6.4.5 Criteria Development

The U.S. EPA (1980d) derived criteria for the protection of aquatic life by means of two approaches. The first was a maximum 'not-to-exceed' level based on acute toxicity data, and the second was a 24-hour average level based on chronic effect data. For PCP, the maximum 'not-to-exceed' criterion was based on the acute LC₅₀ for the most sensitive species tested - coho salmon (55 ug/L). The 24-hour average criterion was based on the chronic growth inhibition threshold of 3.2 ug/L for sockeye salmon. The U.S. EPA (1980d) appears to have misinterpreted the study by Webb and Brett (1973) on sockeye salmon. Careful review of this paper shows that the estimated highest no-effect concentration threshold for growth inhibition was 1.61 ug/L PCP. The highest observed no-effect concentration for growth inhibition was 1.84 ug/L PCP (Webb and Brett 1973).

The calculated criterion using the lowest mean acute LC₅₀ value of 55 ug/L for coho salmon multiplied by the standard application factor of 0.01 for persistent, cumulative contaminants (Section 1.4) would be 0.55 ug/L.

In recognition that the threshold concentration for growth inhibition in sockeye salmon is about 1.5-2 ug/L, which borders the effect/no-effect concentration range, it would appear that the criterion calculated from coho salmon data would provide the required level of protection from chronic effects. It is, therefore, recommended that PCP not exceed 0.5 ug/L to protect against impaired growth in fish.

TABLE 6-1: PHYSICAL PROPERTIES OF PENTACHLOROPHENOL
(adapted from Jones 1981)

CAS No.	Compound	Commercial utility	Formula	Molecular Weight	Boiling point ^a (760 mm or as stated), °C	Melting point ^a (°C)	Dissociation constant ^b at 25°C, K _a
87865	PCP	Yes	C ₆ HCl ₅ O	266.34	309-310(754)	191	1.2x10 ⁻⁵
131522	NaPCP	Yes	C ₆ Cl ₅ ONa	288.36			

Compound	pK ^{c,e}	pK ^d	Water Solubility ^e (moles/L)	Density ^{a,f}	Vapour Pressure ^g @°C	Log P ^j	Appearance
PCP	4.8	5.00	5.6x10 ⁻⁵	1.978 ^{22/4}	3.2x10 ⁻⁴ mm @ 30C ^h 40mm @ 211.2 C 5.0x10 ⁻⁶ mm @ 19°C ⁱ	5.01	Dark coloured flakes and sublimed needle crystals

^a Weast (1974)
^b Doedens (1967)
^c Pearce and Simpkins (1968)
^d Farquharson et al. (1958)
^e NRCC (1982), A review of the relation of solubility of PCP to pH and temperature is provided by NRCC (1982). At 25°C, log S = 1.41 pH -6.15; at 5°C, log S = 1.43 pH -6.89, where S = solubility (g/L)

^f Density is relative to water, the superscript indicates the temperature of the liquid and the subscript the temperature of the water to which the density is referred.
^g Sax (1975)
^h Arsenault (1976)
ⁱ Dobbs and Grant (1980)
^j Leo et al. (1971)

TABLE 6-2: SOLUBILITY OF PENTACHLOROPHENOL AND SODIUM
PENTACHLORPHENATE IN WATER (MONSANTO EUROPE SA 1976;
DOW CHEMICAL COMPANY 1976; FIRESTONE 1977; VERSCHUEREN
1977)

Temperature °C	PCP (pure) (mg/L)	NaPCP (commercial) (g/100 g)
0	5	
5		19
15	12	30
20	14*	
25		33
30	20	

* Windholz (1976) lists the solubility as 80 mg/L. In natural waters, PCP will be primarily present as an anion and its solubility will depend on cationic composition of the water. Anionic PCP is more soluble than undissociated PCP (U.S. EPA 1979).

TABLE 6-3a: CONCENTRATIONS (ppb) OF PENTACHLOROPHENOL IN UNFILTERED WATER, SURFACE FILM AND SURFICIAL SEDIMENT FROM FOUR STATIONS IN THE BAY OF QUINTE (from Fox and Joshi 1984)

	Stations			
	3	4	5	6
Surface film	0.810	0.460	0.538	0.116
Water	0.090	0.010	0.017	not detected
Sediment (dry weight basis)	86	21	62	45

TABLE 6-3b: PENTACHLOROPHENOL CONCENTRATIONS (ppb) FILTERED WATER AND IN DRY SEDIMENT FROM A CONTAMINATED MISSISSIPPI LAKE (from Pierce and Victor 1978)

<u>Date</u>	<u>Sites</u> A	B	C ^a	D
PCP Spill, December 1974				
August 11, 1976				
water ^b	11	0.1	0.1	0.1
sediment ^c	857	429	520	142
October 22, 1976				
water	dry	0.3	0.3	1
sediment	166	994	389	212
PCP Spill, December 1976				
January 5, 1977				
water	81	24	25	16
sediment	277	239	150	170
February 22, 1977				
water	147	-	29	-
sediment	-	1,518	-	-
April 27, 1977				
water	16	5	5	5
sediment	4	250	238	132

a Anaerobic sediment

b Average of triplicate values, ng/ml

c Average of duplicate values, ng/g air-dried sediment

TABLE 6-4: BIOCONCENTRATION FACTORS AND DEPURATION RATES FOR PENTACHLOROPHENOL IN FRESHWATER BIOTA

	BCF	Depuration	Reference
<u>Chlorella fusca</u>	1,250	-	1
Sunfish - muscle	>9-214	-	2
- liver	176-3,510	-	2
<u>Lepomis macrochirus</u>	10-350	rapid, some persistence after 16 days	3*
- muscle	500	-	3**
- gills	1,500	-	**
- liver	8,000	-	**
Bass - muscle	351	-	2
- liver	6,000	-	2
Catfish - muscle	55-513	-	2
- liver	402-5,780	-	2
<u>Carassius auratus</u>	1,000	$T_{1/2} = 10$ h	4
<u>Fundulus similis</u>	53 ($T_{1/2}$ for uptake = 25 h)	$T_{1/2} = 4.7$ days	5
<u>Salmo gairdneri</u>	200-240 (somewhat higher BCF in liver and gall bladder)	-	6
<u>Pimephales promelas</u>	770	-	7*
<u>Poecilia reticulata</u>	500 1,300 -	$T_{1/2} = 30$ days	8* 8** 9
<u>Leuciscus idus melanotus</u>	1,140	-	1
Fish, snails and crustaceans	>100	-	10
<u>Ictalurus nebulosus</u>	15,000	-	11
<u>Perca flavescens</u>	9,100	-	11
Leech	5,000	-	11
Chironomid	60	-	11
<u>Cladophora</u>	400	-	11
Fish (calculated)	4,910 3,620 1,120	- - clearance rate = $1.2 \times 10^{-3} \text{ h}^{-1}$	12* 7** 13*, 14*
Fish (calculated)	302 338 220	- - clearance rate = $9.7 \times 10^{-3} \text{ h}^{-1}$	12** 7*** 13**, 14**

- 1 Freitag et al. (1982)
- 2 Pierce and Victor (1978)
- 3 Pruitt et al. (1977)
- *lab test
- **in contaminated lake
- 4 Kobayashi and Akitake (1975)
- 5 Trujillo et al. (1982)
- 6 Nilimi and McFadden (1982)
- 7 Veith et al. (1979)
- *measured
- **calculated (log P = 5.01)
- ***calculated (log P = 3.80)

- 8 Saarikoski and Viluksela (1982)
- *measured
- **calculated
- 9 Ahling and Jernelov (1969)
- 10 Fox and Hodson (1978)
- 11 Fox and Joshi (1984)
- 12 Mackay (1982)
- *log P = 5.01
- **log P = 3.80
- 13 Neely et al. (1974)
- *log P = 5.01
- **log P = 3.80
- 14 Neely (1979) (see text for assumptions)
- *log P = 5.01
- **log P = 3.80

TABLE 6-5: SUMMARY OF AQUATIC FATE OF PENTACHLOROPHENOL
(after U.S. EPA 1979)

Environmental Process	Summary Statement	Rate	Half Life	U.S. EPA's Confidence of Data
<u>Degradation Processes</u>				
*Photolysis	- of some importance in neutral to alkaline conditions, particularly in shallow, clear waters	-	hours to days in 1 m water at neutral or high pH; weeks to months in other conditions	high
*Biodegradation	- reported in aquatic conditions and in bacterial cultures; favoured by high temperatures and aerobic conditions.	rate is variable in laboratory studies but, in general, $T_{1/2} < 100$ d; may persist for years in organic rich sediments		high
Chemical Degradation	- oxidation and hydrolysis reactions are probably insignificant	-	-	low
<u>Transport Processes</u>				
*Sorption	- important based on log P of 5.01 (undissociated PCP); sorption more favoured under acidic conditions; sediment enrichment observed in contaminated environments	-	-	high
Volatilization	- probably of minor importance in shallow waters at pH < 5; of negligible importance under neutral or alkaline conditions	-	in shallow, 23°C water @ pH 4, $T_{1/2} = 6.3$ d; @ pH 6, $T_{1/2} = 130$ d; negligible at higher pH	medium
Bioaccumulation	- measured BCFs range from 10 to 15,000 in fish, highest values in liver whole body and muscle BCF $\leq 1,000$ in fish, usually ≤ 500 for muscle; calculated BCFs based on log P of 5.01 are higher than measured values; BCF in algae 400-1,250, in invertebrates 60-5,000	uptake rates rapid to moderate (hours to days)	$T_{1/2}$ usually 10 h to ~5 d for depuration	high

Probable overall environmental half-life < 3.5 months (anaerobic conditions) to years in organic rich sediments

*Probable dominant processes in removal and degradation

TABLE 6-6: PRIMARY ACUTE TOXICITY DATA FOR PENTACHLOROPHENOL

Isomer Evaluated	Species	Method ¹	Test Laboratory Water Quality					Laboratory	Reference
			Individual Results (ug/L)	Geometric Mean (ug/L)	Mean pH	Mean Temp. (°C)	Hardness (as CaCO ₃ mg/L)		
PCP	<u>Cladoceran Daphnia magna</u>	48 hr-LC ₅₀ ,S,U	680		8.0	22	173	E,G&G Bionomics, Mass.	LeBlanc 1980
		48 hr-LC ₅₀ ,S,U	260		-	20	HW	Central TNO Lab.,	Canton &
		48 hr-LC ₅₀ ,S,U	240		-	20	HW	Dept. of Biol.,	Adema 1978
		48 hr-LC ₅₀ ,S,U	400		-	20	HW	Delft, Nether.	"
		48 hr-LC ₅₀ ,S,U	400		-	20	HW	"	"
		48 hr-LC ₅₀ ,S,U	790		-	20	HW	"	"
		48 hr-LC ₅₀ ,S,M	600		-	20	HW	Central TNO Lab, Dept. of Biol., Delft, Nether.	Adema 1978
		48 hr-LC ₅₀ ,S,M	1,050	490	8.0	-	HW	Div. of Tech. Delft, Nether.	Adema & Vink 1981
	<u>Daphnia pulex</u>	48 hr-LC ₅₀ ,S,U	2,000		-	20	HW	Central TNO Lab., Dept. of Biol., Delft, Nether.	Canton &
			2,000	2,000	-	20	HW		Adema 1978
	Aquatic Oligochaetes								
	<u>Limnodrilus hoffmeisteri</u>	96 hr-LC ₅₀ ,S,U	305	305	7.0	10	5.3	E.V.S. Consult. Tox. Lab., N. Vcwr.	Chapman <u>et al.</u> 1982 ³
	<u>Branchiura sowerbyi</u>	96 hr-LC ₅₀ ,S,U	259	259	7.0	10	5.3	"	"
	<u>Tubifex tubifex</u>	96 hr-LC ₅₀ ,S,U	351	351	7.0	10	5.3	"	"

TABLE 6-6: PRIMARY ACUTE TOXICITY DATA FOR PENTACHLOROPHENOL (Cont'd)

Isomer Evaluated	Species	Method ¹	Individual Results (ug/L)	Geometric Mean (ug/L)	Test Laboratory Water Quality			Laboratory	Reference
					Mean pH	Mean Temp. (°C)	Hardness (as CaCO ₃ mg/L)		
PCP	<u>Quistadrilus multisetosus</u>	96 hr-LC ₅₀ ,S,U	527	527	7.0	10	5.3	E.V.S. Consult. Tox. Lab., N. Vcwr.	Chapman et al. 1982 ³
	<u>Spirosperma nikolskyi</u>	96 hr-LC ₅₀ ,S,U	906	906	7.0	10	5.3	"	"
	<u>Spirosperma ferox</u>	96 hr-LC ₅₀ ,S,U	397	397	7.0	10	5.3	"	"
	<u>Stylodrilus heringianus</u>	96 hr-LC ₅₀ ,S,U	582	582	7.0	10	5.3	"	"
	<u>Rhyacodrilus montana</u>	96 hr-LC ₅₀ ,S,U	693	693	7.0	10	5.3	"	"
	<u>Varichaeta pacifica</u>	96 hr-LC ₅₀ ,S,U	970	970	7.0	10	5.3	"	"
	Snail <u>Lymnaea acuminata</u>	96 hr-LC ₅₀ ,S,U	180	170	7.9	18	210	K.L.D.A.V. College	Gupta and Rao 1982 ^{2,3,4}
		96 hr-LC ₅₀ ,S,U	160		7.9	18	210		
	<u>Lymnaea stagnalis</u>	48 hr-LC ₅₀ ,S,M	300	269	8.0	-	HW	Div. of Tech. Delft, Nether.	Adema & Vink 1981
		96 hr-LC ₅₀ ,S,M	240		8.0	-	HW		
	Goldfish <u>Carassius auratus</u>	96 hr-LC ₅₀ ,FT,M	210		7.2	25	220	Univ. of Minn.	Adelman & Smith 1976 ³
		96 hr-LC ₅₀ ,Ft,M	220		7.2	25	220	"	
		96 hr-LC ₅₀ ,FT,M	230		7.2	25	220	"	
		96 hr-LC ₅₀ ,FT,M	210		7.2	25	220	"	
		96 hr-LC ₅₀ ,FT,M	170		7.2	25	220	"	

TABLE 6-6:

PRIMARY ACUTE TOXICITY DATA FOR PENTACHLOROPHENOL (Cont'd)

Isomer Evaluated	Species	Method ¹	Individual Results (ug/L)	Geometric Mean (ug/L)	Test Laboratory Water Quality			Laboratory	Reference
					Mean pH	Mean Temp. (°C)	Hardness (as CaCO ₃ mg/L)		
PCP	<u>Carassius auratus</u>	96 hr-LC ₅₀ , FT, M	170		7.2	25	220	Univ. of Minn.	Adelman & Smith 1976
		96 hr-LC ₅₀ , FT, M	220		7.2	25	220	"	"
		96 hr-LC ₅₀ , FT, M	230		7.2	25	220	"	"
		96 hr-LC ₅₀ , FT, M	240		7.2	25	220	"	"
		96 hr-LC ₅₀ , FT, M	240		7.2	25	220	"	"
		96 hr-LC ₅₀ , FT, M	200		7.2	25	220	"	"
		96 hr-LC ₅₀ , FT, M	190		7.2	25	220	"	"
		96 hr-LC ₅₀ , FT, M	290		7.2	25	220	"	"
		96 hr-LC ₅₀ , FT, M	300		7.2	25	220	"	"
		96 hr-LC ₅₀ , FT, M	200		7.2	25	220	"	"
		96 hr-LC ₅₀ , FT, M	250		7.2	25	220	"	"
		96 hr-LC ₅₀ , S, U	60		-	24	SW	U.S. Bureau of Sport Fish & Wildlife	Inglis & Davis 1972
		96 hr-LC ₅₀ , S, U	60		-	24	MW		"
		96 hr-LC ₅₀ , S, U	50	178	-	24	HW		"
	<u>Rainbow Trout Salmo gairdneri</u>	96 hr-LC ₅₀ , S, U	52		-	11	-	Columbia Nat. Fish. Res. Laboratory	Johnson & Finley 1980
		96 hr-LC ₅₀ , S, U	96		7.0	12	47	Pulp & Paper Res. Inst., Pt. Claire, PQ	PPRIC 1979
		96 hr-LC ₅₀ , S, U	75		-	-	-	-	Bentley et al. 1975
		96 hr-LC ₅₀ , S, U	92		-	-	-	-	Davis & Hoos 1975
		96 hr-LC ₅₀ , S, U	85		7.0	12	51.5	EPS, Vcvr. Ref. Tox.	
		96 hr-LC ₅₀ , S, U	89		7.0	12	47.0		

TABLE 6-6:

PRIMARY ACUTE TOXICITY DATA FOR PENTACHLOROPHENOL (Cont'd)

Isomer Evaluated	Species	Method ¹	Test Laboratory Water Quality					Laboratory	Reference
			Individual Results (ug/L)	Geometric Mean (ug/L)	Mean pH	Mean Temp. (°C)	Hardness (as CaCO ₃ mg/L)		
PCP	<u>Salmo gairdneri</u>	96 hr-LC ₅₀ ,S,U	92		7.0	12	5.0	Study, 6 labs in the Vcwr./ Victoria area	"
		96 hr-LC ₅₀ ,S,U	44		5.7	10	4.0		"
		96 hr-LC ₅₀ ,S,U	69		7.0	10	10.0		"
		96 hr-LC ₅₀ ,S,U	130		7.7	15	-	Waste Treat Tech. Ctr., Burlington	Guo <u>et al.</u> 1979
		96 hr-LC ₅₀ ,S,U	150		8.0	15	145	IEC BEAK Mobile Tox. Lab, Marathon Ont.	IEC BEAK 1983 ^{2,3}
		96 hr-LC ₅₀ ,S,U	220		8.0	15	145		
		96 hr-LC ₅₀ ,S,U	180		8.0	15	145		
		96 hr-LC ₅₀ ,S,U	190		8.0	15	145		
		96 hr-LC ₅₀ ,S,U	80		7.5	15	42	IEC BEAK Mobile Tox. Lab, Terrace Bay, Ont.	IEC BEAK 1982 ^{2,3}
		96 hr-LC ₅₀ ,S,U	80		7.5	15	42		
		96 hr-LC ₅₀ ,S,U	90		7.5	15	42		
		96 hr-LC ₅₀ ,S,U	90		7.5	15	42		
		96 hr-LC ₅₀ ,FT,U	213	97	8.2	15	365	Dept. Zool., Univ. Guelph	Fogels & Sprague 1977 ³
	<u>Fathead Minnow</u> <u>Pimephales promelas</u>	96 hr-LC ₅₀ ,FT,M	200		7.2	25	220	Minn. Agric. Exper. Stn., Univ. of Minn	Adelman & Smith 1976 ³
		96 hr-LC ₅₀ ,FT,M	180		7.2	25	220		
		96 hr-LC ₅₀ ,FT,M	220		7.2	25	220		
		96 hr-LC ₅₀ ,FT,M	180		7.2	25	220		
		96 hr-LC ₅₀ ,FT,M	190		7.2	25	220		
		96 hr-LC ₅₀ ,FT,M	210		7.2	25	220		
		96 hr-LC ₅₀ ,FT,M	220		7.2	25	220		
		96 hr-LC ₅₀ ,FT,M	180		7.2	25	220		
		96 hr-LC ₅₀ ,FT,M	190		7.2	25	220		

TABLE 6-6:

PRIMARY ACUTE TOXICITY DATA FOR PENTACHLOROPHENOL (Cont'd)

Isomer Evaluated	Species	Method ¹	Test Laboratory Water Quality					Laboratory	Reference
			Individual Results (ug/L)	Geometric Mean (ug/L)	Mean pH	Mean Temp. (°C)	Hardness (as CaCO ₃ mg/L)		
PCP	<u>Pimephales promelas</u>	96 hr-LC ₅₀ ,FT,M	190		7.2	25	220	Minn. Agric. Exper. Stn., Univ. of Minn.	Adelman & Smith 1976 ³
		96 hr-LC ₅₀ ,FT,M	240		7.2	25	220	"	"
		96 hr-LC ₅₀ ,FT,M	200		7.2	25	220	"	"
		96 hr-LC ₅₀ ,FT,M	200		7.2	25	220	"	"
		96 hr-LC ₅₀ ,FT,M	190		7.2	25	220	"	"
		96 hr-LC ₅₀ ,FT,M	270		7.2	25	220	"	"
		96 hr-LC ₅₀ ,FT,M	230		7.2	25	220	"	"
		96 hr-LC ₅₀ ,FT,M	263		-	-	-	US EPA, Duluth, Minnesota	Cardwell <u>et al.</u> 1976
		96 hr-LC ₅₀ ,S,U	600		5.9	22	-	US EPA, Env. Res. Centre	Mattson <u>et al.</u> 1976
		96 hr-LC ₅₀ ,FT,M	194		8.0	15	-	Minn. Agric. Exper. Stn., Univ. Minn.	Ruesink & Smith 1975 ³
		96 hr-LC ₅₀ ,FT,M	314		8.0	25	-		
		96 hr-LC ₅₀ ,FT,M	221		7.5	23	45	US EPA, Env. Res. Lab., Duluth, Minn.	Phipps <u>et al.</u> 1981 ³
		96 hr-LC ₅₀ ,FT,M	230		7.5	23	45		
	<u>Bluegill Lepomis macrochirus</u>	96 hr-LC ₅₀ ,S,U	205	222	-	20	-	Columbia Nat. Fish. Res. Lab.	Johnson & Finley 1980
		96 hr-LC ₅₀ ,S,U	60		-	-	-	-	Bentley <u>et al.</u> 1975
		96 hr-LC ₅₀ ,S,U	77		-	-	-	-	
		96 hr-LC ₅₀ ,S,M	260		7.4	19	-	Dept. Biology, Univ S. Miss.	Pruitt <u>et al.</u> 1977 ²
		96 hr-LC ₅₀ ,S,M	305		7.4	19	-		

TABLE 6-6:

PRIMARY ACUTE TOXICITY DATA FOR PENTACHLOROPHENOL (Cont'd)

Isomer Evaluated	Species	Method ¹	Individual Results (ug/L)	Geometric Mean (ug/L)	Test Laboratory Water Quality			Laboratory	Reference
					Mean pH	Mean Temp. (°C)	Hardness (as CaCO ₃ mg/L)		
PCP	<u>Lepomis macrochirus</u>	96 hr-LC ₅₀ ,S,U	20		-	24	HW	US Bureau of Sport Fish. & Wildlife	Inglis & Davis 1972
		96 hr-LC ₅₀ ,S,U	32	79	-	15	-	Columbia Nat. Fish. Res. Lab.	Johnson & Finley 1980
	<u>Coho Salmon Oncorhynchus kisutch</u>	96 hr-LC ₅₀ ,S,U	89		7.0	10	15	EPS Vcwr. Std. Ref. Tox. Study, 6 labs Vcwr./Victoria area	Davis & Hoos 1975
		96 hr-LC ₅₀ ,S,U	34	55	7.0	10	5.5		
	<u>Sockeye Salmon Oncorhynchus nerka</u>	96 hr-LC ₅₀ ,S,U	120		7.7	8	47	"	Davis & Hoos 1975
		96 hr-LC ₅₀ ,S,U	46		7.2	13	85	"	
		96 hr-LC ₅₀ ,FT,U	58	68	6.8	15	-	Fish. Res. Bd. Cda., Pacific Bio. Stn., Nanaimo	Webb & Brett 1973
	<u>Channel Catfish Ictalurus punctatus</u>	96 hr-TLm,S	430		-	25	-	-	Clemens & Sneed 1959
		96 hr-LC ₅₀ ,S,U	68	171	-	20	-	Columbia Nat. Fish. Res. Lab.	Johnson & Finley 1980

TABLE 6-6:

PRIMARY ACUTE TOXICITY DATA FOR PENTACHLOROPHENOL (Cont'd)

Isomer Evaluated	Species	Method ¹	Individual Results (ug/L)	Test Laboratory Water Quality				Laboratory	Reference
				Geometric Mean (ug/L)	Mean pH	Mean Temp. (°C)	Hardness (as CaCO ₃ mg/L)		
PCP	<u>Chinook Salmon</u> <u>Oncorhynchus tshawytscha</u>	96 hr-LC ₅₀ ,FT,U	72		7.0	12	54	Minst. of Rec. & Consv, Victoria, B.C.	Iwama & Greer 1979
		96 hr-LC ₅₀ ,S,U	68	70	-	10	-	Columbia Nat. Fish. Res. Lab.	Johnson & Finley 1980
	<u>Brook Trout</u> <u>Salvelinus fontinalis</u>	96 hr-LC ₅₀ ,FT,M	128	128	-	-	-	US EPA, Duluth, Minnesota	Cardwell <u>et al.</u> 1976
		96 hr-LC ₅₀ ,FT,M	217		7.0	25	124	Dept of Fish & Wild Oregon State Univ.	Anderson & Weber 1975
	<u>Guppy</u> <u>Poecilia reticulata</u>	96 hr-LC ₅₀ ,S,M	720 880 450		8.0 8.0 8.0	- - -	HW HW HW	Div of Tech Delft, Nether. "	Adema & Vink 1981 "
		96 hr-LC ₅₀ ,SemiS,M	43		5.0	26	90	Dept. Zoology	Saarikoski &
		96 hr-LC ₅₀ ,SemiS,M	117		6.0	26	90	Univ. of	Viluksela 1981
		96 hr-LC ₅₀ ,SemiS,M	442		7.0	26	90	Helsinki,	"
		96 hr-LC ₅₀ ,SemiS,M	911	470	8.0	26	90	Finland	"

¹Terms: FT = flow-through bioassay, Semi S.= Static bioassay with solution replacement, S = static bioassay, U = test tank concentrations unmeasured, M = test tank concentrations measured, SW = water of low hardness
MW = water of medium hardness, HW = water of high hardness

²Conductivity reported

³Alkalinity reported

⁴Major ions reported

TABLE 6-7: SECONDARY ACUTE TOXICITY DATA FOR PENTACHLOROPHENOL

Isomer Evaluated	Species	Method ¹	Results (ug/L)	Test Laboratory Water Quality			Laboratory	Reference
				Mean pH	Mean Temp. (°C)	Mean Hardness (as CaCO ₃ mg/L)		
PCP	Snail							
	<u>Australorbis</u>	6 hr-TLM,S,U	1,800	-	-	-	-	Seiffer & Schoof 1967
	<u>glabratus</u>	6 hr-LC ₉₅ ,S,U	11,100	-	-	-	-	
	<u>Australorbis</u> sp.	48 hr-LC ₉₄ ,S,U	920	-	-	-	-	Vallejo-Freire <u>et al.</u> 1954
		48 hr-LC ₁₀₀ ,S,U	2,300	-	-	-	-	
	<u>Australorbis</u>	Stream Field Study	8,800	-	-	-	-	Berry <u>et al.</u> 1950
	<u>glabratus</u>	Killed 95%, 2.4 km downstream in 6 hr. flow rate dose						
	Lymnaeid Snails							
	<u>Pseudosuccinea</u>	24 hr-LC ₁₀₀ ,S,U	2,300				Florida Agric. Exp. Stn., Fla.	Batte <u>et al.</u> 1951
	<u>columella</u>							
	<u>Fossaria cubensis</u>	24 hr-LC ₁₀₀ ,S,U	2,300	-	-	-	"	"
	Chironomidae	1 hr-LC ₁₀₀ ,S,U	4,600	7.6	16	-	-	Goodnight 1942
	Aquatic Oligochaete							
	<u>Tubifex tubifex</u>	24 hr-LC ₅₀ ,S,U	286	7.5	20	-	Dept. of Zoology Eastern Illinois Charleston	Whitley 1968
		24 hr-LC ₅₀ ,S,U	619	8.5	20	-		"
		24 hr-LC ₅₀ ,S,U	1,294	9.5	20	-		"
	Rainbow Trout							
	<u>Salmo gairdneri</u>	48 hr-LC ₅₀ ,S,U	157	-	-	-	-	Alabaster 1957
		4 hr-LC ₁₀₀ ,S,U	924	-	12.8	-	U.S. Fish & Wild. Serv., Ann Arbor, Michigan	Applegate <u>et al.</u> 1957

TABLE 6-7: SECONDARY ACUTE TOXICITY DATA FOR PENTACHLOROPHENOL (Cont'd)

Isomer Evaluated	Species	Method ¹	Results (ug/L)	Test Laboratory Water Quality			Laboratory	Reference
				Mean pH	Mean Temp. (°C)	Mean Hardness (as CaCO ₃ mg/L)		
PCP	Rainbow Trout <u>Salmo gairdneri</u>	48 hr-LC ₅₀ ,FT,M	160	-	12	-	Dept. of Fish & Wild., Oregon State University	Chapman 1969
	Steelhead Trout <u>Salmo gairdneri</u>	60 hr-LC ₅₀ ,S,M	230	-	10	-	"	"
	Guppy <u>Poecilia reticulata</u>	48 hr-LC ₅₀ ,S,M	1,050	8.0	-	HW	Div. of Tech. Delft, Nethlds.	Adema & Vink 1981
		48 hr-LC ₅₀ ,S,M	1,050	8.0	-	HW	"	"
		48 hr-LC ₅₀ ,S,M	820	8.0	-	HW	"	"
		Caused Mortality	920	-	-	-	N. Carolina State College, Raleigh	Springer 1957
		1450 min.-LC ₉₄	1,800	-	-	-	-	Klock 1957
		200 min.-LC ₁₀₀	3,700	-	-	-	-	"
		90 min.-LC ₁₀₀	7,400	-	-	-	-	"
		40 min.-LC ₁₀₀	13,800	-	-	-	-	"
		25 min.-LC ₁₀₀	23,100	-	-	-	-	"
		24 hr-LC ₄₀ ,S,U	333	-	26	80	Dept. of Biol. Sciences, Purdue Univ., Indiana	Crandall & Goodnight 1959 ³
		21-38 min.-LC ₅₀ ,S,U	924	5.9	26	80	"	"
		72-93 min.-LC ₅₀ ,S,U	924	7.5	26	80	"	"
		24 hr-LC ₅₀ ,S,U	924	8.9	26	80	"	"

TABLE 6-7: SECONDARY ACUTE TOXICITY DATA FOR PENTACHLOROPHENOL (Cont'd)

Isomer Evaluated	Species	Method ¹	Results (ug/L)	Test Laboratory Water Quality			Laboratory	Reference
				Mean pH	Mean Temp. (°C)	Mean Hardness (as CaCO ₃ mg/L)		
PCP	<u>Brown Trout</u> <u>Salmo trutta</u>	48 hr-LC ₅₀ ,S,U	157	-	-	-	-	Alabaster 1957
		48 hr-LC ₅₀ ,FT,M	160	-	18	-	Dept. of Fish & Wild., Oregon State Univ.	Chapman 1969
	<u>White Crappie</u> <u>Pomoxis annularis</u>	Caused Mortality	52-69	-			N. Carolina State College, Raleigh	Springer 1957
	<u>Spotfin Shiner</u> <u>Notropis</u> <u>spilopterus</u>	18 min.-TLm,S,U	4,600	-	-	-	-	Van Horn 1943
		74 min.-TLm,S,U	920	-	-	-	-	"
		234 min.-TLm,S,U	360	-	-	-	-	"
	<u>Bluntnose Minnow</u> <u>Pimephales notatus</u>	21 min.-TLm,S,U	4,600	-	-	"		
		80 min.-TLm,S,U	920	-	-	-	-	"
		248 min.-TLm,S,U	360	-	-	-	-	"
	<u>Emerald Shiner</u> <u>Notropis</u> <u>atherinoides</u>	16 min.-TLm,S,U	4,600	-	-	-	-	"
		87 min.-TLm,S,U	920	-	-	-	-	"
		418 min.-TLm,S,U	360	-	-	-	-	"
		Lethal Dose	180	-	-	-	-	Van Horn & Balch 1955
		7.6 hr-LC ₁₀₀ ,S,U	460	-	-	-	-	"
		102 hr-LC ₆₉ ,S,U	90	-	-	-	-	"

TABLE 6-7: SECONDARY ACUTE TOXICITY DATA FOR PENTACHLOROPHENOL (Cont'd)

Isomer Evaluated	Species	Method ¹	Results (ug/L)	Test Laboratory Water Quality			Laboratory	Reference
				Mean pH	Mean Temp. (°C)	Mean Hardness (as CaCO ₃ mg/L)		
PCP	Bluegill <u>Lepomis macrochirus</u>	24 hr-LC ₅₀ ,S,U	50	-	24	SW	U.S. Bureau of Sport Fish & Wild.	Inglis & Davis 1972
		24 hr-LC ₅₀ ,S,U	40	-	24	MW	"	"
		24 hr-LC ₅₀ ,S,U	50	-	24	HW	"	"
		48 hr-LC ₅₀ ,S,U	30	-	24	SW	"	"
		48 hr-LC ₅₀ ,S,U	30	-	24	MW	"	"
		48 hr-LC ₅₀ ,S,U	40	-	24	HW	"	"
		48 hr-TLm,S,U	920	-	-	-	-	Turnbull <u>et al.</u> 1954
		8 hr-LC ₁₀₀ ,S,U	920	-	17	-	-	Applegate <u>et al.</u> 1957
	Goldfish <u>Carassius auratus</u>	48 hr-LC ₅₀ ,S,U	170	-	24	SW	U.S. Bureau of Sport Fish & Wildlife	Inglis & Davis 1972
		48 hr-LC ₅₀ ,S,U	80	-	24	MW	"	"
		48 hr-LC ₅₀ ,S,U	110	-	24	HW	"	"
		72 hr-LC ₅₀ ,S,U	80	-	24	SW	"	"
		72 hr-LC ₅₀ ,S,U	70	-	24	MW	"	"
		72 hr-LC ₅₀ ,S,U	60	-	24	HW	"	"
		21 hr-LC ₅₀ ,S,U	340	-	-	-	U.S. EPA, Duluth Minnesota	Cardwell <u>et al.</u> 1976
	Sea Lamprey <u>Petromyzon marinus</u>	4 hr-LC ₁₀₀ ,S,U	924	-	12.8	-	U.S. Fish & Wild. Serv., Ann Arbor Michigan	Applegate <u>et al.</u> 1957

TABLE 6-7: SECONDARY ACUTE TOXICITY DATA FOR PENTACHLOROPHENOL (Cont'd)

Isomer Evaluated	Species	Method ¹	Results (ug/L)	Test Laboratory Water Quality			Laboratory	Reference
				Mean pH	Mean Temp. (°C)	Mean Hardness (as CaCO ₃ mg/L)		
PCP	Bluegill <u>Lepomis macrochirus</u>	24 hr-LC ₅₀ ,S,U	50	-	24	SW	U.S. Bureau of Sport Fish & Wild.	Inglis & Davis 1972
		24 hr-LC ₅₀ ,S,U	40	-	24	MW		"
		24 hr-LC ₅₀ ,S,U	50	-	24	HW		"
		48 hr-LC ₅₀ ,S,U	30	-	24	SW		"
		48 hr-LC ₅₀ ,S,U	30	-	24	MW		"
		48 hr-LC ₅₀ ,S,U	40	-	24	HW		"
		48 hr-TLm,S,U	920	-	-	-	-	Turnbull <u>et al.</u> 1954
		8 hr-LC ₁₀₀ ,S,U	920	-	17	-	-	Applegate <u>et al.</u> 1957
	Goldfish <u>Carassius auratus</u>	48 hr-LC ₅₀ ,S,U	170	-	24	SW	U.S. Bureau of Sport Fish & Wildlife	Inglis & Davis 1972
		48 hr-LC ₅₀ ,S,U	80	-	24	MW		"
		48 hr-LC ₅₀ ,S,U	110	-	24	HW		"
		72 hr-LC ₅₀ ,S,U	80	-	24	SW		"
		72 hr-LC ₅₀ ,S,U	70	-	24	MW		"
		72 hr-LC ₅₀ ,S,U	60	-	24	HW		"
		21 hr-LC ₅₀ ,S,U	340	-	-	-	U.S. EPA, Duluth Minnesota	Cardwell <u>et al.</u> 1976
	Sea Lamprey <u>Petromyzon marinus</u>	4 hr-LC ₁₀₀ ,S,U	924	-	12.8	-	U.S. Fish & Wild. Serv., Ann Arbor Michigan	Applegate <u>et al.</u> 1957

TABLE 6-7: SECONDARY ACUTE TOXICITY DATA FOR PENTACHLOROPHENOL (Cont'd)

Isomer Evaluated	Species	Method ¹	Results (ug/L)	Test Laboratory Water Quality			Laboratory	Reference
				Mean pH	Mean Temp. (°C)	Mean Hardness (as CaCO ₃ mg/L)		
PCP	<u>Fathead Minnow</u> <u>Pimephales promelas</u>	260 min.-LT ₅₀ ,S,U	920	7.5	10	-	Dept. of Biol. Sciences, Purdue Univ., Indiana	Crandall & Goodnight 1959 "
		81 min.-LT ₅₀ ,S,U	920	7.5	18	-		
		46 min.-LT ₅₀ ,S,U	920	7.5	26	-		
		21 hr-LC ₅₀ ,S,U	310	-	-	-	U.S. EPA, Duluth, Minnesota	Cardwell <u>et al.</u> 1976
	<u>Atlantic Salmon</u> <u>Salmo salar</u>	24 hr-LC ₅₀ ,FT,U	800	-	6-15	-	Fish. & Marine Serv., St. Andrew, New Brunswick	Peterson 1976
	<u>Coho Salmon</u> <u>Oncorhynchus kisutch</u>	Median Resistance Time	2,800	-	10	-	Fish. Res. Bd. Can. Biol. Stn., Nanaimo	Alderice 1963
	<u>Brook Trout</u> <u>Salvelinus fontinalis</u>	24 hr-LC ₅₀ ,S,U	300	-	-	-	U.S. EPA, Duluth, Minnesota	Cardwell <u>et al.</u> 1976

¹Terms: S = static bioassay, FT = flow-through bioassay, U = test tank concentrations unmeasured
M = test tank concentrations measured, SW = water of low hardness,
MW = water of medium hardness, HW = water of high hardness

²Conductivity reported

³Alkalinity reported

TABLE 6-8: PRIMARY CHRONIC TOXICITY DATA FOR PENTACHLOROPHENOL

Isomer Evaluated	Species	Method ¹	Test Conc. Ranges (ug/L)	Conc. of Lowest Chronic Effect (ug/L)	Test Laboratory Water Quality			Laboratory	Reference
					Mean pH	Mean Temp. (°C)	Hardness (as CaCO ₃ mg/L)		
PCP	<u>Cladoceran Daphnia magna</u>	21 day-Life Cycle, FT, M	180-320	250	8.0	20	HW	Div. of Tech Delft, Neth.	Adema 1978
			340-400	370	8.0	20	HW		Adema & Vink 1981
	<u>Mollusc Lymnaea stagnalis</u>	16 day-Early Life Stage, FT, M	50-130	90	8.0	-	HW	Div. of Tech Delft, Neth.	Adema & Vink 1981
	<u>Fathead Minnow Pimephales promelas</u>	32 day-Early Life Stage, FT, M	45-73	59	7.5	25	46	U.S. EPA Env. Res. Lab Duluth, Minn.	Holcombe et al. 1982 ³
	<u>Rainbow Trout Salmo gairdneri</u>	28 day-Early Life Stage, FT, M	9-14	11	8.0	10.3	-	Great Lakes Biolimnology Laboratory Burlington, Ont.	Hodson and Blunt 1981 ²
					8.1	14.8	-		
					7.9	20.1	-		
					7.8	5.4	-		
					7.8	5.4	-		
			19-37	28	7.9	11.7	-		

TABLE 6-8: PRIMARY CHRONIC TOXICITY DATA FOR PENTACHLOROPHENOL (Cont'd)

Isomer Evaluated	Species	Method ¹	Test Conc. Ranges (ug/L)	Conc. of Lowest Chronic Effect (ug/L)	Test Laboratory Water Quality			Laboratory	Reference
					Mean pH	Mean Temp. (°C)	Hardness (as CaCO ₃ mg/L)		
PCP	Steelhead Trout <u>Salmo gairdneri</u>	30 day-Early Life Stage, Ft, M	37-9	21	7.8	10.0	-	Western Fish Toxic. Stn., U.S. EPA, Corvallis	Chapman & Shumway 1977
	Sockeye Salmon <u>Oncorhynchus nerka</u>	56 day-EC ₅₀ , Growth Inhib.	-	1.61	6.8	15	-	Fish. Res. Bd. Can., Pacific Biol. Stn., Nanaimo	Webb & Brett 1973
		56 day-EC ₅₀ , Conversion Eff.	-	1.66	6.8	15	-		"

¹Terms: FT = flow-through bioassay, Semi S.= Static bioassay with solution replacement, S = static bioassay, U = test tank concentrations unmeasured, M = test tank concentrations measured, SW = water of low hardness MW = water of medium hardness, HW = water of high hardness

²Conductivity reported

³Alkalinity reported

TABLE 6-9: SECONDARY CHRONIC TOXICITY DATA FOR PENTACHLOROPHENOL

Isomer Evaluated	Species	Method ¹	Results (ug/L)	Test Laboratory Water Quality			Laboratory	Reference
				Mean pH	Mean Temp. (°C)	Mean Hardness (as CaCO ₃ mg/L)		
PCP	<u>Cladoceran</u> <u>Daphnia magna</u>	14 day-LC ₅₀ ,FT,M	440	8.0	20	HW	Div. of Tech. Delft, Nether.	Adema 1978
		14 day-LC ₅₀ ,FT,M	460	8.0	20	HW	"	"
		21 day-LC ₅₀ ,FT,M	480	8.0	20	HW	"	"
		21 day-LC ₅₀ ,FT,M	510	8.0	20	HW	"	"
		21 day-LC ₅₀ ,FT,M	400	8.0	20	HW	"	"
		21 day-LC ₅₀ ,FT,M	470	8.0	20	HW	"	"
		21 day-LC ₅₀ ,FT,M	430	8.0	20	HW	"	"
		21 day-LC ₅₀ ,FT,M	490	8.0	20	HW	"	"
		21 day-LC ₅₀ ,FT,M	170	8.0	20	HW	"	"
		21 day-LC ₅₀ ,FT,M	190	8.0	20	HW	"	"
		96 hr-LC ₅₀ ,S,M	600	8.0	-	HW	"	Adema & Vink, 1981
		7 day-LC ₅₀ ,FT,M	400	8.0	-	HW	"	"
		14 day-LC ₅₀ ,FT,M	400	8.0	-	HW	"	"

TABLE 6-9: SECONDARY CHRONIC TOXICITY DATA FOR PENTACHLOROPHENOL (cont'd)

Isomer Evaluated	Species	Method ¹	Results (ug/L)	Test Laboratory Water Quality			Laboratory	Reference
				Mean pH	Mean Temp. (°C)	Mean Hardness (as CaCO ₃ mg/L)		
PCP	Crayfish <u>Astacus fluviatilis</u>	8 day-LC ₅₀ ,S.U.	9,000	6.5	13	-	-	Kaila & Saarikoski, 1977
		8 day-LC ₅₀ ,S.U.	53,000	7.5	13	-	-	"
	Snail <u>Lymnaea stagnalis</u>	16 day-LC ₅₀ ,FT,M	180	8.0	-	HW	Div. of Tech. Delft, Nether.	Adema & Vink 1981
	Rainbow Trout <u>Salmo gairdneri</u>	20 day-11% growth inhibition	28	-	-	-	Dept. of Fish and Wildl. Oregon State Univ.	Chapman, 1969
		20 day-18% growth inhibition	28	-	-	-	"	"
		21 day-19% growth inhibition	28	-	-	-	"	"
		28 day-12% growth inhibition	28	-	-	-	"	"
		38 day-18% growth inhibition	28	-	-	-	"	"
		41 day-9% growth inhibition	9.2	-	-	-	"	"
		41 day-LC ₁₀₀	46	-	-	-	"	"

TABLE 6-9: SECONDARY CHRONIC TOXICITY DATA FOR PENTACHLOROPHENOL (cont'd)

Isomer Evaluated	Species	Method ¹	Results (ug/L)	Test Laboratory Water Quality			Laboratory	Reference
				Mean pH	Mean Temp. (°C)	Mean Hardness (as CaCO ₃ mg/L)		
PCP	<u>Rainbow Trout</u> <u>Salmo gairdneri</u>	92 day-9% growth inhibition	7.4	-	-	-	-	Matida <u>et al.</u> 1970
		28 day-27% growth inhibition	7.4	-	-	-	-	
		10 day-LC ₅₀ ,FT,U	213	8.2	15	365	Dept. of Zool. Univ. of Guelph	Fogels and Sprague 1977 ³
	<u>Goldfish</u> <u>Carassius auratus</u>	14 day-LC ₅₀ ,S,U	175	-	-	-	U.S. EPA Duluth, Minn.	Cardwell <u>et al.</u> 1976
		11 day-LC ₅₀ ,FT,M	210	7.6	23	210	Dept. of Entom. Univ. of Minn.	Adelman & Smith 1976 ³
	<u>Atlantic Salmon</u> <u>Salmo solar</u>	24 hr-altered temp. preference	46	-	6-15		Fisher. & Marine Serv., St. Andrews New Brunswick	Peterson, 1976
	<u>Brook Trout</u> <u>Salvelinas fontinalis</u>	9 day-LC ₅₀ ,S,U	109	-	-	-	U.S. EPA Duluth, Minn.	Cardwell <u>et al.</u> 1976
	<u>Bluegill</u> <u>Lepomis macrochirus</u>	14 day, LC ₅₀ ,S,U	174	-	-	-	"	"
	<u>Guppy</u> <u>Poecilia reticulata</u>	90 day, LC ₄₅	462	8.5	-	165	Dept. of Biol. Sci. Purdue Univ.	Crandall & Goodnight, 1962 ³

TABLE 6-9: SECONDARY CHRONIC TOXICITY DATA FOR PENTACHLOROPHENOL (cont'd)

Isomer Evaluated	Species	Method ¹	Results (ug/L)	Test Laboratory Water Quality			Laboratory	Reference
				Mean pH	Mean Temp. (°C)	Mean Hardness (as CaCO ₃ mg/L)		
PCP	<u>Fathead Minnow</u> <u>Pimephales promelas</u>	8 day-LC ₅₀ ,FT,M	200	7.5	23	45	U.S. EPA Envir. Research Lab. Duluth, Minn.	Phipps <u>et al.</u> 1981
		8 day-LC ₅₀ ,Ft,M	220	7.5	23	45		
		14 day-LC ₅₀ ,S,U	141				U.S. EPA, Duluth, Minn.	Cardwell <u>et al.</u> 1976
		11 day-LC ₅₀ ,FT,M	210	7.6	25	210	Dept. of Entom. Univ. of Minn.	Adelman & Smith 1976 ³
	<u>Green Sunfish</u> <u>Lepomis cyanellus</u>	Avoidance Behav. (repelled)	20,000	-	-	-	-	Summerfelt & Lewis 1976

¹Terms: FT = flow-through bioassay, S = static bioassay, U = test tank concentrations unmeasured, M = test tank concentrations measured

²Conductivity reported

³Alkalinity reported

TABLE 6-10: PLANT VALUES FOR PENTACHLOROPHENOL

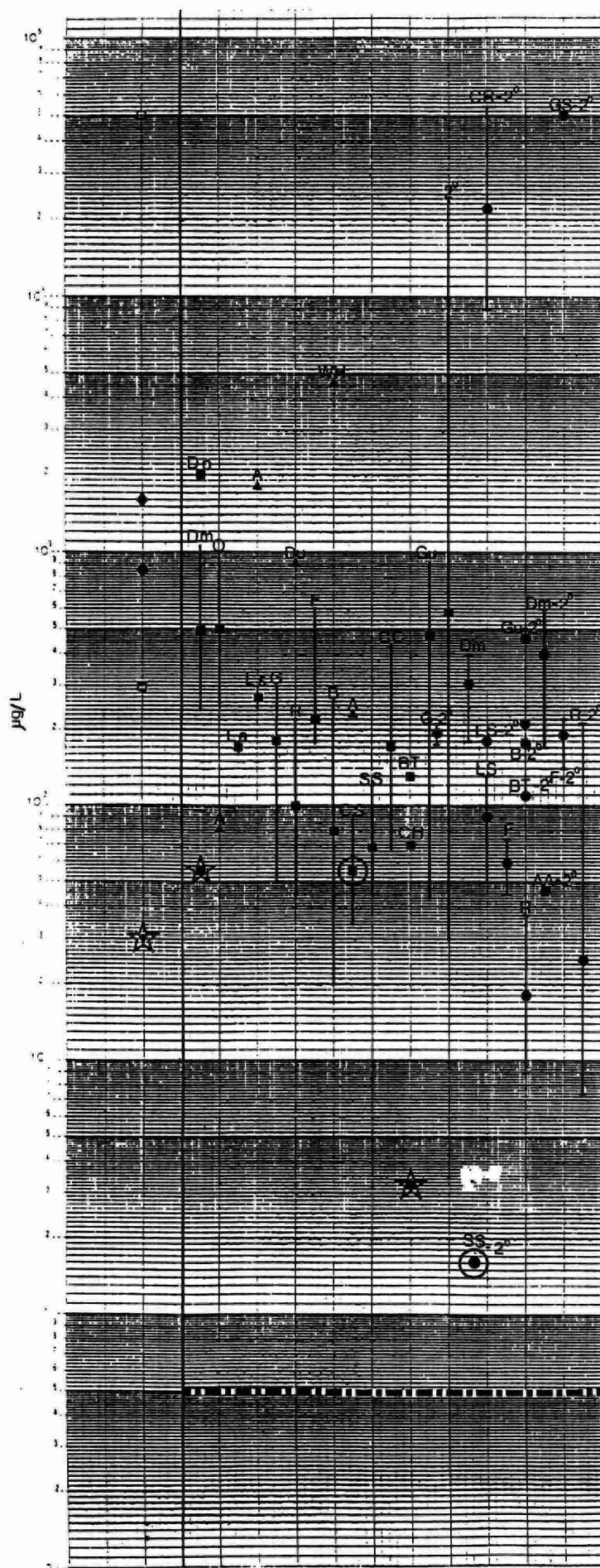
Isomer Evaluated	Species	Method ¹	Results (ug/L)	Test Laboratory Water Quality			Laboratory	Reference
				Mean pH	Mean Temp. (°C)	Mean Hardness (as CaCO ₃ mg/L)		
PCP	Green Algae <u>Chlorella pyrenoidosa</u>	Chlorosis (growth) 72 hr-EC ₁₀₀	7.5	7.0	25	-	Civil Eng. Dept., Univ. of Texas	Huang & Gloyna 1969
		96 hr-EC ₅₀ S,M	7,000	8.0	-	HW	Div. of Tech., Delft, Nether.	Adema & Vink 1981
	<u>Scenedesmus quadricauda</u>	96 hr-EC ₅₀ S,M	80	8.0	-	HW	"	"
	Water Hyacinth <u>Crassipes eichornia</u>	Minimum to cause effect	4,600	-	-	-	-	Hirsch 1942
		Dose to kill	73,900	-	-	-	-	"
	Duckweed <u>Lemna minor</u>	Chlorosis 48-hour, EC ₅₀	800	5.1	25	-	Dept. of Agric., Oxford Univ., England	Blackman <u>et al.</u> 1955
	Blue-Green Algae <u>Cylindrospermum licheniforme</u>	3 day-toxic, S,U	1,800	-	-	-	"	Palmer & Maloney 1955
	<u>Microcystis aeruginosa</u>	3 day-toxic, S,U	1,800	-	-	-	"	"
	Green Alga <u>Scenedesmus obliquus</u>	7 day-partially, S,U, toxic	1,800	-	-	-	"	"

TABLE 6-10: PLANT VALUES FOR PENTACHLOROPHENOL (Cont'd)

Isomer Evaluated	Species	Method ¹	Results (ug/L)	Test Laboratory Water Quality			Laboratory	Reference
				Mean pH	Mean Temp. (°C)	Mean Hardness (as CaCO ₃ mg/L)		
PCP	<u>Diatoms Gomphonema parvulum</u>	7 day-partially, S,U, toxic	1,800	-	-	-	Dept. of Agric., Oxford Univ., England	Palmer & Maloney 1955
	<u>Nitzschia palea</u>	3 day-toxic, S,U	1,800	-	-	-	"	"

¹Terms: S = static bioassay, U = test vessel concentrations unmeasured, HW = water with high hardness
M = test vessel concentrations measured.

Taste and Odour
Criteria



CODES

- ◆ Odour Threshold
- ▼ Taste Threshold
- Acute Toxicity
- Chronic Toxicity
- ▲ Plant Data
- ★ Tainting (Fish Flesh)
- ☆ EPA Criteria
- Soviet Criteria
- 2° Secondary Data
- Recommended Criterion
- Vertical bars represent data ranges
- Critical Values in Criteria Selection

Test Species

- WH Water Hyacinth
- A Alga
- Dm Daphnia magna
- Dp Daphnia pulex
- O Oligochaetes
- F Fathead Minnow
- B Bluegill
- GS Green Sunfish
- G Goldfish
- R Rainbow Trout
- BT Brook Trout
- CH Chinook Salmon
- CS Coho Salmon
- AA Atlantic Salmon
- SS Sockeye Salmon
- Gu Guppy
- CC Channel Catfish
- La Lymnaea accuminata
- Ls Lymnaea stagnalis
- CR Crayfish

Routine detection limit
MOE, December 1983:
50 ng/L.

FIGURE 6-1:
PENTACHLOROPHENOL
TOXICITY AND CRITERIA SUMMARY
Recommended Criterion 0.5 µg/L

7.0 STRUCTURE-ACTIVITY CONSIDERATIONS IN AQUATIC TOXICITY

A few studies have been undertaken to characterize relationships between physicochemical properties and toxicity of CP's. Results of these studies should not be used to attempt quantitative predictions of toxicity to aquatic biota in general, because the applicability of these relationships to a diversity of species has not been tested. Nonetheless, structure-toxicity relationships provide valuable insight into the important parameters influencing toxicity.

Liu et al. (1982) studied structure-toxicity relationships of an array of CP's using Bacillus cultures isolated from activated sludge. Because several CP's were studied using one test species under the same experimental conditions, several interesting observations on the interrelationships between toxicity, the degree of chlorination and the position of chlorine substituents on the phenol ring could be made. The results of this investigation supported the generalization that toxicity increases with the degree of chlorination; however, it was clearly shown that the position of chlorine is also an important determining factor. Para-substituted phenols were usually more toxic than ortho-isomers. Also, when both meta positions are chlorinated, toxicity was strongly enhanced. Thus, 2-CP was less toxic than 4-CP. Among DCP's, 2,6-DCP was the least toxic (two ortho chlorines) and 3,5-DCP the most toxic (two meta chlorines). Among TCP's, 2,3,5-TCP (two meta chlorines) was more toxic than either 2,4,6-TCP or 2,3,6-TCP. Liu et al. (1982) also found that the 2,6 chlorination dominates over the toxicity enhancement caused by the 3,5 chlorination, as illustrated by the toxicity of TTCP isomers to Bacillus. Thus, 2,3,5,6-TTCP was less toxic than 2,3,4,5-TTCP. The authors noted that this could explain why PCP, which has both double ortho and double meta substitutions, was less toxic than the lower chlorinated 2,3,4,5-TTCP.

It is impossible to show most of the structure-toxicity relationships described by Liu et al. (1982) using the data available on toxicity to aquatic biota presented in this report. However, the qualitative structure-toxicity relationships observed in Bacillus species may also apply to the aquatic toxicology of CP's.

Quantitative structure-activity correlations (QSAR's) for toxicities of CP's to aquatic biota were developed by McLeese et al. (1979), Konemann and Musch (1981) and Saarikoski and Viluksela (1982). These QSAR's were based on octanol-water partition

coefficients, which measure lipophobicity, and on Δ pKa values (pKa of phenol minus pKa of the chlorinated phenol) which account for the dissociation of acidic compounds. Results were generally comparable among these studies, but the best correlations were derived by Saarikoski and Viluksela (1982) using LC₅₀ values for guppy at pH 7:

$$\begin{aligned}\log (1/\text{LC}_{50}) &= 0.60 \log P - 0.31, r = 0.983 \\ \log (1/\text{LC}_{50}) &= 0.36 \text{ pKa} + 0.69, r = 0.888\end{aligned}$$

Chlorination increases both the acidity and the lipophobicity of CP's. Saarikoski and Viluksela (1982) also developed a QSAR applicable to normal environmental pH levels of 6 to 8:

$$\log (1/\text{LC}_{50\text{pH}}) = \log (1/\text{LC}_{50\text{HA}}) - \log (4^{\text{pH}-\text{pKa}} + 1)$$

where LC₅₀ pH is the LC₅₀ value at specified pH, LC_{50HA} is the LC₅₀ value for the unionized CP, pH is the pH of the test solution, and pKa is the log of the ionization constant of the CP.

The correlation between toxicity and log P at pH 6 and pH 7, observed by Saarikoski and Viluksela, was unexpected because the log P values used were for undissociated CP's. The more acidic CP's (e.g., PCP) are mostly in the phenate form even at pH 6. Phenate ions have octanol-water partition coefficients that are at least three orders of magnitude less than those of the unionized forms (Hansch and Leo 1979). Thus, apparent log P values are highly dependent on pH, as quantified by Kaiser and Valdmanis (1982) for PCP.

Saarikoski and Viluksela (1982) found that acidity affects the toxicity of CP's in two ways. First, toxicity and Δ pKa are positively correlated. Thus, as acidity increases, so does toxicity. The pKa values tabulated for the individual CP's in this report indicate a general increase in acidity with increasing chlorination. Second, ionization of CP's tends to decrease their toxicity because phenate ions do not penetrate biological membranes as readily as the undissociated molecular forms (e.g., see Holcombe *et al.* 1980). Thus, as the acidity of a CP and the pH of a CP solution increase, the degree of ionization also increases. Correspondingly, toxicity tends to decrease.

Saarikoski and Viluksela (1982) cautioned, however, that the importance of lipophobicity and ionization in determining the toxicity of CP's may be considerably different in different organisms. For example, McLeese et al. (1979), in measuring the toxicity of 23 phenols to shrimp, found only weak correlations between log P, Δ pKa and toxicity.

Sabljić (1983) attempted to develop structure-toxicity correlations for chlorinated organics using an alternate approach called molecular connectivity. CP's were included in the QSAR development. The author stated that this approach is preferable to QSAR's based on physico-chemical data because no empirical measurements or reference tables are required. Toxicity was correlated with a "zero order connectivity index", based on the arrangement of non-hydrogen atoms in the molecule. The derived equations accounted for 84-88% of the variation in the toxicity data.

As more information becomes available on structure-toxicity relationships of CP's, these considerations might be incorporated into the development of criteria for individual isomers.

8.0 RESEARCH NEEDS

During this review, areas where aquatic effect information was found to be lacking were identified. Studies which would improve the chlorophenol data base are listed below:

- Studies should be undertaken using a sensitive Ontario species such as rainbow trout to quantify pH-toxicity relationships for a wide array of CP isomers.
- Tainting thresholds-pH relationships should be determined for MCP, DCP and TCP isomers. These isomers have relatively low tainting thresholds, and bioaccumulation may be affected by the degree of dissociation which is in turn controlled by pH conditions.
- Toxicity studies with CP's should more clearly define test conditions (water quality), particularly since pH influences CP ionization and toxicity.
- **Monochlorophenol**
More chronic fish or invertebrate studies are required. Only one study is presently available and the species used was not the most sensitive. Daphnia magna reproductive or rainbow trout early life stage studies are recommended.
- **Dichlorophenol**
More chronic fish or invertebrate data for isomers other than 2,4-DCP is required. It is recommended that D. magna or rainbow trout studies be conducted.
- **Trichlorophenol**
Tainting data are required for 2,4,5-TCP. Good chronic data is needed for 2,4,5- and 2,4,6-TCP. It is recommended that rainbow trout be used for tainting work and D. magna or rainbow trout be selected for primary chronic studies.
- **Tetrachlorophenol**
Tainting data is required for the two main isomers, 2,3,4,6- and 2,3,5,6-TTCP. Good chronic data is also required for both of these isomers. It is recommended that rainbow trout be used for tainting work and D. magna or rainbow trout be selected for primary chronic studies.

- **Pentachlorophenol**

Both acute and chronic toxicity data bases are fairly complete. Tainting thresholds are higher than toxic thresholds so additional flavour impairment studies should be given low priority. There is conflicting information as to the effects of PCP on algae; further algal toxicity work should be conducted to determine PCP effects.

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APPENDIX I

Guidelines for Toxicity Data Used in Criteria Development

APPENDIX I: GUIDELINES FOR TOXICITY DATA USED IN CRITERIA DEVELOPMENT DATA

A. GENERAL GUIDELINES

- Only consider freshwater species native or introduced to North America.
- Discard data without sufficient information to indicate that acceptable test procedures were used. Do not assume that all published data are acceptable.
- Discard questionable data (e.g., no control treatment existed, distilled water was used in controls, etc.).
- Discard data on formulated mixtures and emulsifiable concentrates of the substance, but not necessarily data on technical grade material (although toxic impurities in technical grade material must be considered (e.g., PCP)).
- Data on flavour impairment responses are considered separately from toxicity data.

B. GUIDELINES FOR SELECTION OF PRIMARY ACUTE TOXICITY DATA

- Primary acute tests will be based on accepted procedures such as outlined by the Environmental Protection Service (1980), and the American Society for Testing and Materials (1980a,b).
- Results of acute tests should be based on endpoints and lengths of exposure appropriate to the life stage of the species tested. Therefore, only the following kinds of data on acute toxicity to aquatic animals are used:
 - 48-hour LC_{50}/EC_{50} values based on immobilization and 48-hour LC_{50} values for first-instar (less than 24 hours old) cladocerans.

- 96-hour EC₅₀ values on immobilization, loss of equilibrium or both, and 96-hour LC₅₀ values for aquatic animals, except for cladocerans, midges and animals whose behaviour or physiology allows them to avoid exposure to toxicant (e.g., air-breathing molluscs and unionid clams).
- If the acute toxicity of the substance is related to a water quality characteristic such as hardness, the acute toxicity criterion should be derived based on that water quality characteristic. Criteria would be derived for these toxicants based on specific ranges of water quality conditions.
- All acute toxicity information not meeting the guidelines for summary data selection, but acceptable under the general guidelines, is considered secondary acute data.

C. GUIDELINES FOR SELECTION OF PRIMARY CHRONIC TOXICITY DATA

- Only results of flow-through chronic tests where concentrations of toxicant in the test solutions were measured are accepted. A possible exception would be daphnid chronic tests where there has been solution renewal.
- Results of any chronic test in which survival, growth or reproduction among the controls was unacceptably low are not used.
- Chronic values should be based on endpoints and lengths of exposure appropriate to the species. Therefore, only the results of the following kinds of chronic toxicity tests are used:
 - Life-cycle toxicity tests consisting of exposures of each of several groups of individuals of a species to a different concentration of the toxicant throughout a life cycle. To ensure that all life stages and life processes are exposed, the test should begin with embryos or newly hatched young less than 48 hours old (less than 24 hours old for daphnids), continue through maturation and reproduction, and with fish should end not less than 21 days (90 days for salmonids) after the hatching of the next generation. For fish,

data are obtained and analyzed on survival and growth of adults and young, maturation of males and females, embryos spawned per female, embryo viability (salmonids only) and hatchability. For daphnids, data are obtained and analyzed on survival and young per female.

- Partial life-cycle toxicity tests consisting of exposures of each of several groups of individuals of a species of fish to a different concentration of the toxicant through most portions of a life cycle. Partial life-cycle tests are conducted with fish species that require more than a year to reach sexual maturity, so that the test can be completed in less than 15 months, but still expose all major life stages to the toxicant. Exposure to the toxicant begins with immature juveniles at least 2 months prior to active gonad development, continues through maturation and reproduction, and ends not less than 21 days (90 days for salmonids) after the hatching of the next generation. Data should be obtained and analyzed on survival and growth of adults and young, maturation of males and females, embryos spawned per female, embryo viability (salmonids only) and hatchability.
- Early-life-stage toxicity tests consisting of 21 to 32 days (60 days post-hatch for salmonids) exposures of the early life stages of a species of fish from shortly after fertilization through embryonic, larval, and early juvenile development. Data should be obtained and analyzed on survival and growth.
- All chronic toxicity information not meeting the guidelines for primary data selection, but acceptable under the general guidelines, is considered secondary chronic data.

APPENDIX II

Taste and Odour Impairment by Chlorophenols in Drinking Water

IMPAIRMENT OF ODOUR AND TASTE IN WATER

Monochlorophenols

A summary of odour and taste thresholds for MCP's in drinking water is presented in Table A-1. The threshold for taste of all MCP's in water is low (0.1 ug/L; Dietz and Traud 1978). Odour thresholds vary considerably, but are as low as 0.33 ug/L for 2-CP at 30°C. Because these aesthetic criteria are lower than the recommended criterion of 10 ug/L for the protection of aquatic life, taste and odour thresholds should be considered for domestic water supplies.

Dichlorophenols

A summary of odour and taste thresholds for DCP's in drinking water is presented in Table A-2. Taste thresholds are low, and range from 0.04 ug/L for 2,3-DCP to 0.5 ug/L for 2,5-DCP (Dietz and Traud 1978). Odour thresholds vary considerably, depending on the specific isomer and on water temperature, but are as low as 0.33 ug/L for 2,5-DCP at 30°C. These aesthetic criteria are higher than the recommended criterion of 0.1 ug/L for the protection of aquatic life, therefore, the recommended criterion should protect domestic water supplies from odour and taste impairment.

Trichlorophenols

A summary of odour and taste thresholds for TCP's in drinking water is presented in Table A-3. Taste thresholds are low, and range from 0.5 ug/L for 2,3,6-TCP to 2.0 ug/L for 2,4,6-TCP (Dietz and Traud 1978). Odour thresholds vary considerably, depending on the specific isomer and on water temperature, but are as low as 11 ug/L for 2,4,5-TCP at 25°C. Because some of these aesthetic criteria are below the recommended criterion of 3 ug/L for the protection of aquatic life, taste and odour thresholds should be considered for domestic water supplies.

Tetrachlorophenols

A summary of odour and taste thresholds for TTCP's in drinking water is presented in Table A-4. A taste threshold is available only for 2,3,4,6-TTCP (1 ug/L; Dietz and Traud

1978). Odour thresholds vary with temperature and are as low as 600 ug/L at 20-22°C. The odour thresholds for 2,3,4,6-TTCP is considerably higher than the recommended criterion of 1 ug/L for the protection of aquatic life. However, the taste threshold for 2,3,4,6-TTCP is equal to the recommended criterion, and taste thresholds should be considered for domestic water supplies.

Pentachlorophenol

A summary of odour and taste thresholds for PCP in drinking water is presented in Table A-5. The taste threshold for PCP is 30 ug/L. Odour thresholds vary with temperature and are as low as 857 ug/L at 30°C. Both taste and odour thresholds for PCP are above the recommended criterion of 0.5 ug/L for the protection of aquatic life. Thus, our recommended criterion should protect domestic water supplies from aesthetic impairment by PCP.

TABLE A-1: Organoleptic Water Quality Criteria (ug/L) for Monochlorophenols

Basis		2-CP	3-CP	4-CP	Reference
Odour threshold:	20-22°C	10	50	60	1
	25°C	2	-	250	2
	30°C	0.33	200	33	3
Taste threshold		0.1*	0.1*	0.1*	1

1. Dietz and Traud (1978)
2. Burttschell et al (1959)
3. Hoak (1957)

* Criteria recommended by U.S. EPA

TABLE A-2: Organoleptic Water Quality Criteria (ug/L) for Dichlorophenols

Basis	2,3	2,4	2,5	2,6	3,4	Reference
Odour						
Threshold: 20-22°C	30	40	30	200	100	1
25°C	-	2	-	3	-	2
30°C	-	0.65	0.33	-	-	3
*	-		2			4
Taste	0.04**	0.3**	0.5**	0.2**	0.3**	1
Threshold:		8.0		2.0		2
Soviet						
Criterion (taste/odour)	2	2	2	2	2	5

¹Dietz and Traud (1978)²Burttschell et al. (1959)³Hoak (1957)⁴Zoeteman (1975)⁵Stofen (1973)

* temperature unspecified

** Criteria recommended by U.S. EPA

TABLE A-3: Organoleptic Water Quality Criteria (ug/L) for Trichlorophenols

Basis		2,3,6	2,4,5	2,4,6	Reference
Odour					
Threshold:	20-22°C	300	200	300	1
	25°C	-	11	> 1000	2,3
	30°C	-	-	100	3
Taste Threshold					
		0.5	1.0*	2.0*	1
Soviet Criterion					
	(taste/odour)	0.4	0.4	0.4	4

¹Dietz and Traud (1978)

²Burttschell et al. (1959)

³Hoak (1957)

⁴Stofen (1973)

*Criteria recommended by U.S. EPA

TABLE A-4: Organoleptic Water Quality Criteria (ug/L) for Tetrachlorophenols

Basis		2,3,4,6	Reference
Odour Threshold:	20-22°C	600	1
	30°C	915	2
Taste		1*	1

¹Dietz and Traud (1978)

²Hoak (1957)

*Criterion recommended by U.S. EPA

TABLE A-5: Organoleptic Water Quality Criteria (ug/L) for Pentachlorophenol

Basis		Criterion	Reference
Odour Threshold:	20-22°C	1600	1
	30°C	857	2
Taste Threshold		30*	1
Soviet Criterion			
(taste/odour):	PCP	300	3
	NaPCP	5000	3

¹Dietz and Traud (1978)

²Hoak (1957)

³Stofen (1973)

*Criterion recommended by U.S. EPA